EXHIBIT D

INTRODUCTION TO ANALYTICAL METHODS

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Exhibit D - Analytical Methods

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1.0 INTRODUCTION

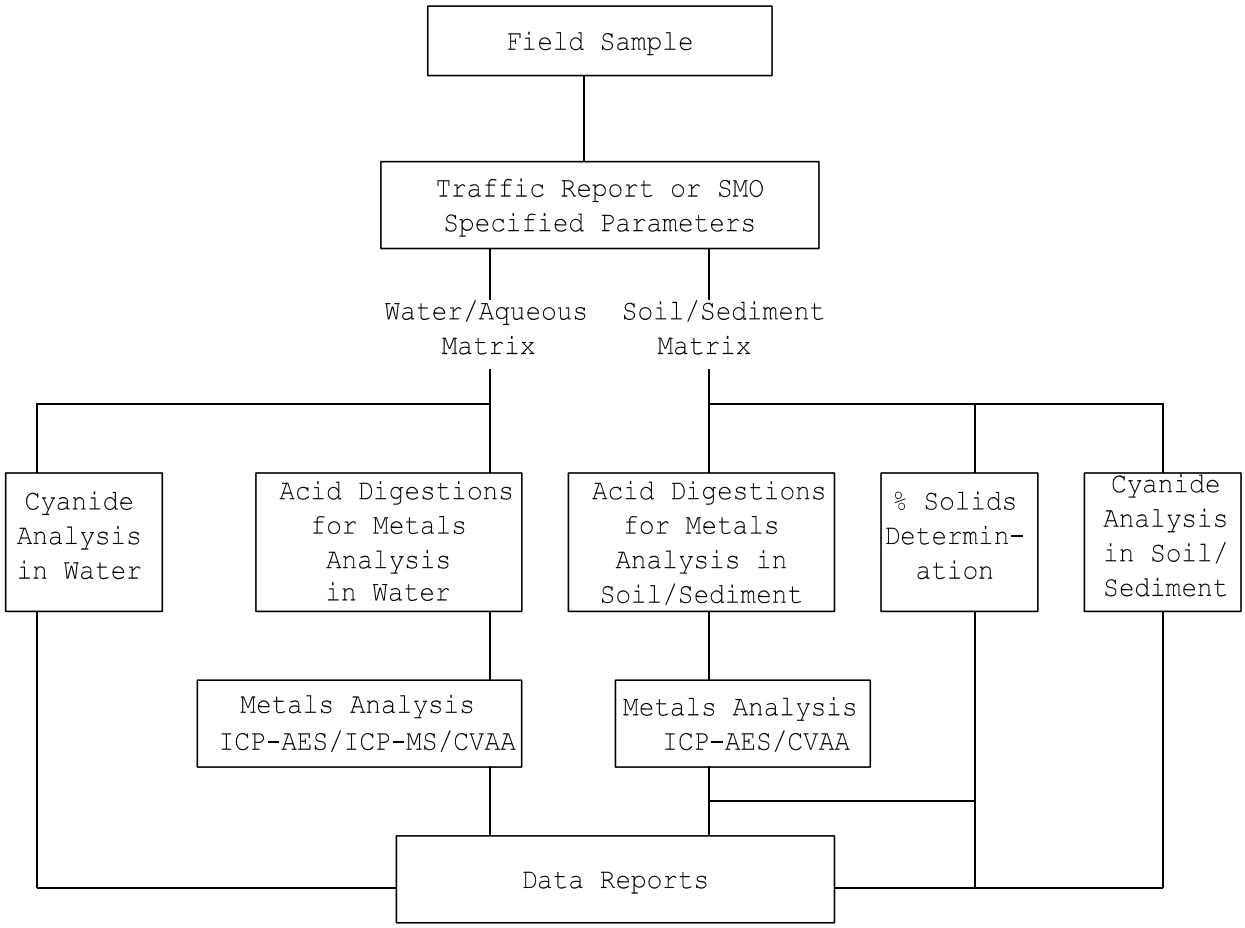
The inorganic analytical service provides a contractual framework for laboratories. This framework applies USEPA Contract Laboratory Program (CLP) analytical methods for the isolation, detection, and quantitative measurement of 23 metals (including mercury) and cyanide in water/ aqueous and/or soil/sediment samples.

The analytical methods that follow are designed to analyze water and sediment/soil from hazardous waste sites for the presence of inorganic analytes contained on the Inorganic Target Analyte List (TAL) (see Exhibit C). The inorganic methods include alternative analysis procedures for some analytes, multiple preparation procedures, and Quality Control (QC) requirements. Analytical techniques in the inorganic methodologies include Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES), Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), Cold Vapor Atomic Absorption Spectroscopy, and Spectrophotometry. Graphite Furnace Atomic Absorption (GFAA) may be requested by the modified analysis clause in the contract.

1.1 Inorganic Methods Flow Chart

Figure 1 outlines the general analytical scheme the Contractor shall follow in performing standard trace metals and cyanide analyses under this contract.

1.2 Figure 1 - Inorganic Methods Flow Chart



1.3 Glassware Cleaning

Lab glassware to be used within the metals analysis must be acid cleaned according to USEPA's manual, Methods for Chemical Analysis of Water and Wastes or an equivalent procedure. An electronic version can be found via USEPA's National Environmental Publications Internet Site (NEPIS) at http://www.epa.gov/cincl.

1.4 Standard Stock Solutions

Stock solutions to be used for preparing instrument or method standards may be purchased or prepared as described in the individual methods of Exhibit D, Section 7 (Reagents and Standards).

1.5 Verification of Aqueous Sample Preservation

1.5.1 At the time of sample receipt, the Contractor shall check the pH of the sample and note in a preparation log if the pH is less than 2 for metals. In addition, it should be noted if the pH is greater than 12 for a cyanide sample. Unless instructed by the USEPA Regional CLP Project Officer (CLP PO), the Contractor shall not perform any pH adjustment action if the sample has not been properly preserved. If the sample has not been properly preserved, contact Sample Management

Office (SMO) for further instructions before proceeding with the preparation and analysis. The Contractor may adjust the pH of a sample for metals if SMO provides written documentation to the Contractor from the USEPA Regional CLP PO or USEPA Office of Superfund Remediation and Technology Innovation (OSRTI) Analytical Services Branch (ASB) Inorganic Program Manager (ASB PM) authorizing the adjustment.

1.5.2 Before preparation is initiated for an aqueous cyanide sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper (which has been pre-moistened with pH 4 acetate buffer solution). If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide. This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through a dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the Sample Delivery Group (SDG) Narrative.

1.6 Percent Solids Determination Procedure

1.6.1 Immediately following the weighing of the sample to be processed for analysis, add 5-10 g of sample to a tared weighing dish. Weigh and record the weight to the nearest 0.01 g.

1.6.2 Place weighing dish plus sample, with the cover tipped to allow for moisture escape, in a drying oven maintained at 103-105°C. Sample handling and drying should be conducted in a well-ventilated area.

1.6.3 Dry the sample overnight (12-24 hours) but no longer than 24 hours. If dried less than 12 hours, it must be documented that constant weight was attained.[1] Remove the sample from the oven and cool in a desiccator with the weighing dish cover in place before weighing. Weigh and record weight to nearest 0.01 g. Do not analyze the dried sample.

1.6.4 Duplicate percent solids determinations are required at the same frequency as other analytical determinations. Duplicate results are to be recorded on Form VI-IN.

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[1]Drying time is defined as the elapsed time in the oven; thus raw data must record time in and out of the oven to document the 12-hour drying time minimum. In the event it is necessary to demonstrate the attainment of constant weight, data must be recorded for a minimum of two repetitive weigh/dry/desiccate/weigh cycles with a minimum of 1-hour drying time in each cycle. Constant weight would be defined as a loss in weight of no greater than 0.01 g between the start weight and final weight of the last cycle.

1.6.5 For the duplicate percent solids determination, designate one sample aliquot as the "original" sample and the other aliquot as the "duplicate" sample. Calculate dry weight using the results of the "original" sample aliquot.

1.6.6 Calculate percent solids by the formula below. The value thus obtained will be reported on the appropriate Forms I and, where applicable, Forms VA-IN and VI-IN. This value will be used for calculating analytical concentration on a dry weight basis.

EQ. 1 Percent Solids

$$\% \text{ Solids} = \frac{\text{Sample Dry Weight}}{\text{Sample Wet Weight}} \times 100$$

1.6.7 If the sample contains less than 50% solids, the Contractor shall notify SMO immediately of the samples impacted. After notification to SMO, the Contractor shall proceed with sample analysis and document the issue in the SDG Narrative.

1.7 Insufficient Sample Volume

If insufficient sample volume (less than the required amount) is received to perform the analysis, the Contractor shall contact the SMO to apprise them of the problem. SMO will contract the Region for instructions. The Region will either approve that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. SMO will notify the Contractor of the Region's decision. The Contractor shall document the Region's decision in the SDG Narrative.

1.8 Sample Mixing

Unless instructed otherwise by the USEPA Regional CLP PO, all samples shall be mixed thoroughly prior to aliquoting for digestion. There is no specific procedure provided herein for homogenization of soil/ sediment samples; however, an effort should be made to obtain a representative aliquot.

1.9 Undiluted Analysis

1.9.1 All samples shall be run undiluted for multi-analyte analysis (i.e., the final product of the sample preparation procedure) unless the dilution adjusted detection limits for all analytes are below the CRQL. When an analyte concentration exceeds the calibrated or linear range, appropriate dilution (but not below the CRQL) and re-analysis is required. The Contractor shall use the least dilution necessary to bring the analyte(s) instrument reading within the upper 75% of the calibrated or linear range and report the highest valid value for each analyte as measured from the undiluted and diluted analyses. Unless the Contractor can submit proof that dilution was required to obtain valid results, both diluted and undiluted sample measurements must be contained in the raw data.

1.9.2 For single analyte analysis, a diluted sample analysis may be the only sample analysis performed if the analyte's instrument result is in the upper 75% of the calibrated or linear range. An undiluted sample analysis does not have to be performed in this case. The sample and its associated matrix spike and duplicate shall initially be run at the same dilution.

1.9.3 All sample dilutions shall be made with reagent water appropriately acidified (except for cyanide) to maintain constant acid strength.

1.10 Dissolved Metals

1.10.1 If dissolved metals are requested by USEPA Regional Offices, the Contractor shall follow the instructions provided on the Traffic Report(s)/Chain of Custody Record(s). If there are no instructions on the Traffic Report/Chain of Custody Record, the Contractor shall digest the samples designated as dissolved metals.

1.10.2 If the Regional Office indicates on the Traffic Report/Chain of Custody Record that a digestion is not to be performed when analyzing field samples for dissolved metals, then a aqueous Laboratory Control Sample (LCSW) and a post-digestion spike sample (hardcopy Form VB-IN and diskette QC codes PDO and PDF) are not required.

1.11 Replicate Exposure

If the Contractor analyzes samples using multiple injections or exposures, the Contractor must use the data obtained from all injections or exposures to calculate the final sample result even if more than the minimum number of injections or exposures are taken.

1.12 Raw Data Requirements

The Contractor is reminded and cautioned that the collection and provision of raw data may or may not be referred to within the individual methods of Exhibit D or the Quality Assurance (QA) protocol of Exhibit E. The raw data deliverable requirements are specified in Exhibit B, Section 2.5.2.3. Raw data collected and provided in association with the performance of analyses under this contract shall conform to the appropriate provisions of Exhibit B.

1.13 Quality Control Samples

If the Sampler designated two (or more) samples as QC for the same matrix, and the QC samples are not specifically labeled with the analysis they are to be used for (dissolved metals and total metals), then the Contractor is to contact SMO to report the issue. SMO shall then contact the Region and notify the Contractor of the Regional decision.

1.14 Safety

The toxicity or carcinogenicity of each reagent used in this SOW has not been precisely defined; however, each chemical compound should be treated as a potential health hazard. From this viewpoint, exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current awareness file of Occupational Safety and Health Administration (OSHA) regulations regarding the safe handling of chemicals specified in this method. A reference file of material handling data sheets should also be made available to all personnel involved in the chemical analysis.

1.15 Pollution Prevention

1.15.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. USEPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, USEPA recommends recycling as the next best option.

1.15.2 For information about pollution prevention that may be applicable to laboratories and research institutions consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street, N.W., Washington D.C., 20036, (202) 872-4477.

1.16 Waste Management

USEPA requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. USEPA urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any sewer discharge permits and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult "The Waste Management Manual for Laboratory Personnel", available from the American Chemical Society at the address listed in Section 1.15.2.

EXHIBIT D - PART A

ANALYTICAL METHODS
FOR
INDUCTIVELY COUPLED PLASMA -
ATOMIC EMISSION SPECTROSCOPY

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Exhibit D - Analytical Methods for ICP-AES

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1.0 SCOPE AND APPLICATION

The following method is an inductively coupled atomic plasma-atomic emission spectroscopy procedure that is used to analyze water, sediment, sludge, and soil samples taken from hazardous waste sites. All metals (except mercury) which are contained in the Inorganic Target Analyte List (TAL) in Exhibit C are quantitated by this Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) method.

2.0 SUMMARY OF METHOD

Water and soil samples are treated with acids and heat or microwave energy to solubilize the metals present. These digestates are then analyzed for trace metals by an atomic emission optical spectroscopic technique. Samples are nebulized and the aerosol that is produced is transported to a plasma torch where excitation occurs. Characteristic atomic-line emission spectra are produced by a radio-frequency inductively coupled plasma. The spectra are dispersed and the intensities of the lines are monitored by a photosensitive device. The signals from the photosensitive device are processed by a computer. A background correction technique is required to compensate for variable background contribution to the spectra of trace elements. Background must be measured adjacent to analyte lines on samples during analysis. The position selected for the background intensity measurement, on either or both sides of the analytical line, will be determined by the complexity of the spectrum adjacent to the analyte line. The position used must be free of spectral interference and reflect the same change in background intensity as occurs at the analyte wavelength measured. Background correction is not required in cases of line broadening where a background correction measurement would actually degrade the analytical result.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Several types of interference effects may contribute to inaccuracies in the determination of trace elements in water and soil/sediments. To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. This is especially true when dissolved solids exceed 1500 milligrams per Liter (mg/L) and when total elements are determined after the appropriate digestion procedures are performed. Several types of interferences are summarized below:

4.1 Spectral Interferences

Spectral interferences can be categorized as: overlap of a spectral line from another element, unresolved overlap of molecular band spectra, background contribution from continuous or recombination phenomena, and/or background contribution from stray light from the line emission of high concentration elements. The first of these effects can be compensated by utilizing a computer correction of the raw data. This would require the monitoring and measurement of the interfering element. The second effect may require selection of an alternate wavelength. The third and fourth effects can usually be compensated by a background correction adjacent to the analyte line. In addition, users of simultaneous multi-element instrumentation must assume the responsibility of verifying the absence of spectral interference from an element that could occur in a sample but for which there is no channel in the instrument array.

4.2 Physical Interferences

Physical interferences are generally considered to be effects associated with the sample nebulization and transport processes. Such properties as change in viscosity and surface tension can cause significant inaccuracies especially in samples which may contain high dissolved solids and/or acid concentrations. The use of a peristaltic pump may minimize these interferences. If these types of interferences are present, they must be reduced by dilution of the sample.

Another problem which can occur from high dissolved solids is salt buildup at the tip of the nebulizer. This affects aerosol flow rate causing instrumental drift. Wetting the argon prior to nebulization, the use of a tip washer, or sample dilution has been used to control this problem. Also, it has been reported that better control of the argon flow rate improves instrument performance. This is accomplished with the use of mass flow controllers.

4.3 Chemical Interferences

Chemical interferences are characterized by molecular compound formation, ionization effects and solute vaporization effects. Normally these effects are not pronounced with the Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) technique; however, if observed they can be minimized by careful selection of operating conditions (that is, incident power, observation position, and so forth), by buffering of the sample, and by matrix matching. These types of interferences can be highly dependent on matrix type and the specific analyte element.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel

6.1.2 Watch glasses

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks (Type A)

6.1.6 Thermometer that covers a range of 0-200°C

6.1.7 Whatman No. 42 filter paper or equivalent

6.1.8 Hot plate, block digester, or other heating source

6.1.9 Equipment and supplies for microwave digestion

6.1.9.1 Whatman No. 41 filter paper (or equivalent)

6.1.9.2 Disposable polypropylene filter funnel

6.1.9.3 Polyethylene bottles, 125 mL, with caps

6.1.9.4 Microwave oven with programmable power settings up to at least 600 watts.

6.1.9.5 The system must use PTFE PFA digestion vessels (120 mL capacity) capable of withstanding pressure of up to 110 (±10) pounds per square inch (psi) [7.5 (±0.7 atm)]. These vessels are capable of controlled pressure relief at pressures exceeding 110 psi.

6.1.9.6 A rotating turntable must be used to ensure homogeneous distribution of microwave radiation within the oven. The speed of the turntable must be a minimum of 3 revolutions per minute (rpm).

6.1.10 Balances - Analytical Balance, 300 gram (g) capacity, and minimum ±0.01 g.

6.2 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) consisting of a computer controlled atomic emission spectrometer with background correction, a radio frequency generator, and a supply of Argon gas, welding grade or better.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Acetic acid - Concentrated (specific gravity 1.06).

7.1.3 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.4 Hydrochloric acid, (1+1) - Add 500 milliliters (mL) conc. HCl (specific gravity 1.19) to 400 mL reagent water and dilute to 1 Liter (L).

7.1.5 Nitric acid - Concentrated (specific gravity 1.41).

7.1.6 Nitric acid, (1+1) - Add 500 mL conc. HNO_3 (specific gravity 1.41) to 400 mL reagent water and dilute to 1 L.

7.1.7 Hydrogen peroxide (30%)

7.1.8 Nitric acid, 5% (v/v) - Add 50 mL conc. HNO_3 to 500 mL reagent water; dilute to 1 L.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased or prepared from reagent grade chemicals or metals. All salts must be dried for 1 hour at 105°C unless otherwise specified.

(CAUTION: Many metal salts are extremely toxic and may be fatal if swallowed. Wash hands thoroughly after handling) Typical stock solution preparation procedures follow.

7.2.2.2 Aluminum solution, stock (1 mL = 100 µg Al) - Dissolve 0.100 grams (g) of aluminum metal in an acid mixture of 4 mL of (1+1) HCl and 1 mL of conc. HNO_3 in a beaker. Warm gently to effect solution. When solution is complete, transfer quantitatively to a liter flask, add an additional 10 mL of (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.3 Antimony solution, stock (1 mL = 100 µg Sb) - Dissolve 0.2669 g $K(SbO)C_4H_4O_6$ in reagent water, add 10 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.4 Arsenic solution, stock (1 mL = 100 µg As) - Dissolve 0.1320 g of As_2O_3 in 100 mL of reagent water containing 0.4 g NaOH. Acidify the solution with 2 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.5 Barium solution, stock (1 mL = 100 µg Ba) - Dissolve 0.1516 g $BaCl_2$ (dried at 250°C for 2 hours) in 10 mL reagent water with 1 mL (1+1) HCl. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.6 Beryllium solution, stock (1 mL = 100 µg Be) - Do not dry. Dissolve 1.966 grams (g) $BeSO_4 \bullet 4H_2O$, in reagent water, add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.7 Cadmium solution, stock (1 mL = 100 µg Cd) - Dissolve 0.1142 g CdO in a minimum amount of (1+1) HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.8 Calcium solution, stock (1 mL = 100 µg Ca) - Suspend 0.2498 g $CaCO_3$ dried at 180°C for 1 hour before weighing in reagent water and dissolve cautiously with a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.9 Chromium solution, stock (1 mL = 100 µg Cr) - Dissolve 0.1923 g of CrO_3 in reagent water. When solution is complete acidify with 10 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.10 Cobalt solution, stock (1 mL = 100 µg Co) - Dissolve 0.1000 g of cobalt metal in a minimum amount of (1+1) HNO_3. Add 10.0 mL (1+1) HCl and dilute to 1000 mL with reagent water.

7.2.2.11 Copper solution, stock (1 mL = 100 µg Cu) - Dissolve 0.1252 g CuO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.12 Iron solution, stock (1 mL = 100 µg Fe) - Dissolve 0.1430 g Fe_2O_3 in a warm mixture of 20 mL (1+1) HCl and 2 mL of conc. HNO_3. Cool, add an additional 5 mL of conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.13 Lead solution, stock (1 mL = 100 µg Pb) - Dissolve 0.1599 g $Pb(NO_3)_2$ in a minimum amount of (1+1) HNO_3. Add 10.0 mL of conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.14 Magnesium solution, stock (1 mL = 100 µg Mg) - Dissolve 0.1658 g MgO in a minimum amount of (1+1) HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.15 Manganese solution, stock (1 mL = 100 µg Mn) - Dissolve 0.1000 g of manganese metal in the acid mixture, 10 mL conc. HCl and 1 mL conc. HNO_3, and dilute to 1000 mL with reagent water.

7.2.2.16 Nickel solution, stock (1 mL = 100 µg Ni) - Dissolve 0.1000 g of nickel metal in 10 mL hot conc. HNO_3, cool and dilute to 1000 mL with reagent water.

7.2.2.17 Potassium solution, stock (1 mL = 100 µg K) - Dissolve 0.1907 g KCl, dried at 110°C, in reagent water. Dilute to 1000 mL.

7.2.2.18 Selenium solution, stock (1 mL = 100 µg Se) - Do not dry. Dissolve 0.1727 g H_2SeO_3 (actual assay 94.6%) in reagent water and dilute to 1000 mL.

7.2.2.19 Silver solution, stock (1 mL = 100 µg Ag) - Dissolve 0.1575 g $AgNO_3$ in 100 mL of reagent water and 10 mL conc. HNO_3. Dilute to 1000 mL with reagent water.

7.2.2.20 Sodium solution, stock (1 mL = 100 µg Na) - Dissolve 0.2542 g NaCl in reagent water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.21 Thallium solution, stock (1 mL = 100 µg Tl) - Dissolve 0.1303 g $TlNO_3$ in reagent water. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.22 Vanadium solution, stock (1 mL = 100 µg V) - Dissolve 0.2297 NH_4VO_3 in a minimum amount of conc. HNO_3. Heat to increase rate of dissolution. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.2.23 Zinc solution, stock (1 mL = 100 µg Zn) - Dissolve 0.1245 g ZnO in a minimum amount of dilute HNO_3. Add 10.0 mL conc. HNO_3 and dilute to 1000 mL with reagent water.

7.2.3 Secondary Dilution Standards

7.2.3.1 Mixed Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with acidified reagent water to obtain the final volume. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 The calibration blank is prepared by diluting 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to 100 mL with reagent water. Prepare a sufficient quantity to be used to flush the system between standards and samples.

7.2.4.2 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentration of the analytes in the CRI shall be at the respective CRQLs. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.4.3 Interference Check Sample (ICS) Solution

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents.

7.2.4.4 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.2.4.5 Mixed Calibration Standard Solutions

7.2.4.5.1 Prepare mixed calibration standard solutions by combining appropriate volumes of the stock solutions in volumetric flasks (see Sections 7.2.4.5.2 through 7.2.4.5.7). Add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl and dilute to 100 mL with reagent water (see Note in Section 7.2.4.5.6). Prior to preparing the mixed standards, each stock solution should be analyzed separately to determine possible spectral interference or the presence of impurities. Care should be taken when preparing the mixed standards that the elements are compatible and

stable. Transfer the mixed standard solutions to a FEP fluorocarbon or unused polyethylene bottle for storage. Fresh mixed standards should be prepared as needed with the realization that concentration can change with aging. Although not specifically required, some typical calibration standard combinations follow.

7.2.4.5.2 Mixed standard solution I - manganese, beryllium, cadmium, lead, and zinc.

7.2.4.5.3 Mixed standard solution II - barium, copper, iron, vanadium, and cobalt.

7.2.4.5.4 Mixed standard solution III - arsenic and selenium.

7.2.4.5.5 Mixed standard solution IV - calcium, sodium, potassium, aluminum, chromium, and nickel.

7.2.4.5.6 Mixed standard solution V - antimony, magnesium, silver and thallium.

NOTE: If the addition of silver to the recommended acid combination results in an initial precipitation, add 15 mL of reagent water and warm the flask until the solution clears. Cool and dilute to 100 mL with reagent water. For this acid combination, the silver concentration should be limited to 2 milligrams per Liter (mg/L). Silver under these conditions is stable in a tap water matrix for 30 days. Higher concentrations of silver require additional HCl.

7.2.4.5.7 Protect all standards from light. Samples, sample digestates, and standards must be stored separately.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedures for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 365 days after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

The maximum holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, linear dynamic range, and interference effects must be investigated and established for each individual analyte line on that particular instrument. All measurements must be within the instrument linear range where correction factors are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Microwave Calibration Procedure

9.2.1 The calibration procedure is a critical step prior to the use of any microwave unit. The microwave unit must be calibrated every six months. The data for each calibration must be available for review during on-site audits. In order that absolute power settings may be interchanged from one microwave unit to another, the actual delivered power must be determined.

9.2.2 Calibration of a laboratory microwave unit depends on the type of electronic system used by the manufacturer. If the unit has a precise and accurate linear relationship between the output power and the scale used in controlling the microwave unit, then the calibration can be a two-point calibration at maximum and 40% power. If the unit is not accurate or precise for some portion of the controlling scale, then a multiple-point calibration is necessary. If the unit power calibration needs a multiple-point calibration, then the point where linearity begins must be identified. For example: a calibration at 100, 99, 98, 97, 95, 90, 80, 70, 60, 50, and 40% power settings can be applied and the data plotted. The non-linear portion of the calibration curve can be excluded or restricted in use. Each percent is equivalent to approximately 5.5-6 watts and becomes the smallest unit of power that can be controlled. If 20-40 watts are contained from 99-100%, that portion of the microwave calibration is not controllable by 3-7 times that of the linear portion of the control scale and will prevent duplication of precise power conditions specified in that portion of the power scale.

9.2.3 The power available for heating is evaluated so that the absolute power setting (watts) may be compared from one microwave to another. This is accomplished by measuring the temperature rise in 1 kilogram (kg) of water exposed to microwave radiation for a fixed period of time. The water is placed in a PTFE beaker (or a beaker that is made of some other material that does not absorb microwave energy) and stirred before measuring the temperature. Glass beakers absorb microwave energy and may not be used. The initial temperature of the water must be between 19 and 25°C. The beaker is circulated continuously through the field for at least two minutes at full power. The beaker is removed from the microwave, the water is stirred vigorously, and the final temperature is recorded. The final reading is the maximum temperature reading after each energy exposure. These measurements must be accurate to ±0.1°C and made within 30 seconds of the end of heating. If more measurements are needed, do not use the same water until it has cooled down to room temperature. Otherwise, use a fresh water sample.

The absorbed power is determined by the following formula:

EQ. 1 Absorbed Power

$$P = \frac{(K)\ (C_p)\ (m)\ (DT)}{t}$$

WHERE, P = The apparent power absorbed by the sample in watts (joules per second).

K = The conversion factor for thermochemical calories per second to watts (=4.184).

C_p = The heat capacity, thermal capacity, or specific heat (cal. g^{-1} $°C^{-1}$) of water (=1.0).

m = The mass of the sample in grams (g).

DT = The final temperature minus the initial temperature (°C).

t = The time in seconds (s).

Using 2 minutes and 1 kg of reagent water, the calibration equation simplifies to:

$$P = (DT)\ (34.87)$$

The microwave user can now relate power in watts to the percent power setting of the microwave.

9.3 Inductively Coupled Plasma - Atomic Emission Spectrometer (ICP-AES) Instrument Calibration Procedure

9.3.1 Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.3.2 The calibration standards shall be prepared as in Section 7.2.4.5.

9.3.3 Calibrate the ICP-AES instruments according to instrument manufacturer's recommended procedures. At least two standards shall be used for ICP-AES calibration. One of the standards shall be a blank.

9.3.4 Any changes or corrections to the analytical system shall be followed by recalibration.

9.4 Initial Calibration Verification (ICV)

9.4.1 Immediately after each of the ICP-AES systems have been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) at each wavelength used.

9.4.2 Only if the ICV solution(s) is(are) not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a

concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

9.4.3 The ICV solution(s) shall be run at each wavelength used for analysis. The values for the ICV shall be reported on Form IIA-IN.

9.5 Continuing Calibration Verification (CCV)

9.5.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported for every wavelength used for the analysis of each analyte, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported for every wavelength used for analysis at the beginning of the run and after the last analytical sample. The analyte concentrations in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near one-half of the calibration standard:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.5.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.5.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.6 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at each wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water/Aqueous Sample Preparation

10.1.3.1 Preparation Method/Code (HW1) (USEPA Method 200.7, December 1982)

Shake sample and transfer 50-100 milliliter (mL) of well-mixed sample to a 250 mL heating vessel, add 2 mL of (1+1) HNO_3 and 10 mL of (1+1) HCl to the sample. Cover with watch glass or similar cover and heat on a hot plate, block digester, or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours or until sample volume is reduced to between 25 and 50 mL, making certain sample does not boil. Cool sample and filter to remove insoluble material.

NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Adjust sample volume to 50-100 mL with reagent water. The sample is now ready for analysis. Concentrations so determined shall be

reported as "total". If volumes less than 100 mL are used, all other reagents shall be reduced appropriately (e.g., if 50 mL is used, reduce reagent volumes by one-half). The final volume of the digestate must equal the initial volume of the sample aliquot.

10.1.3.2 Preparation Method/Code (MW1) (USEPA SW-846 Method 3015)

10.1.3.2.1 A 45 mL aliquot of the sample is measured into PTFE digestion vessels.

10.1.3.2.2 5 mL of concentrated HNO_3 is added to the digestion vessels.

10.1.3.2.3 The caps with the pressure release valves are placed on the vessels hand tight and then tightened, using constant torque, to 12 ft/lbs. The weight of each vessel is recorded to 0.02 gram (g).

10.1.3.2.4 Place 5 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. Venting tubes connect each sample vessel with a collection vessel. Each sample vessel is attached to a clean, double-ported overflow vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave.

10.1.3.2.5 This procedure is energy balanced for five 45 mL water samples (each with 5 mL of acid) to produce consistent conditions. When fewer than five samples are digested, the remaining vessels must be filled with 45 mL of tap, deionized, or reagent water and 5 mL of concentrated nitric acid.

10.1.3.2.6 Newer microwave ovens may be capable of higher power settings which may allow a larger number of samples. If the analyst wishes to digest more than 5 samples at a time, the analyst may use different power settings as long as they result in the same time temperature conditions defined in the power programming for this method.

10.1.3.2.7 The initial temperature of the samples should be 24°C (±1°C). The Preparation Blank (PB) must have 45 mL of deionized water and the same amount (5 mL) of acid that is added to the samples.

10.1.3.2.8 The microwave unit first-stage program must be set to give 545 watts for 10 minutes and the second-stage program to give 344 watts for 10 minutes. This sequence brings the samples to 160°C (±4°C) in 10 minutes and permits a slow rise to 165-170°C during the second 10 minutes.

10.1.3.2.9 Following the 20 minute program, the samples are left to cool in the microwave unit for 5 minutes, with the exhaust fan on. The samples and/or carousel may then be removed from the microwave unit. Before opening the vessels, let cool until they are no longer hot to the touch.

10.1.3.2.10 After the sample vessel has cooled, weigh the sample vessel and compare to the initial weight as reported on the preparation log. Any sample vessel exhibiting a less than or equal to 0.5 g loss into the overflow vessel must have any excess sample from the associated collection vessel added to the original sample vessel before proceeding with the sample preparation.

Any sample vessel exhibiting a greater than 0.5 g loss must be identified in the preparation log and the sample redigested.

10.1.3.2.11 Sample Filtration - The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. The digestates are then filtered into 50 mL glass volumetric flasks through Whatman No. 41 (or equivalent) filter paper and diluted to 50 mL (if necessary). The samples are now ready for analysis. The sample results must be corrected by a factor of 1.11 in order to report final concentration values based on an initial volume of 45 mL. Concentrations so determined shall be reported as "total".

10.1.3.3 Preparation Method/Code (MW2) (ASTM Standard D4309-91)

10.1.3.3.1 A 50 mL aliquot of the sample is measured into PTFE digestion vessels.

10.1.3.3.2 3 mL of concentrated HNO_3 and 2 mL of concentrated HCl is added to the digestion vessels.

10.1.3.3.3 Proceed as in Preparation Method/Code "MW1", Sections 10.1.3.2.3 through 10.1.3.2.11.

10.1.3.3.4 Sample Filtration - The digested samples are shaken well to mix in any condensate within the digestion vessel before being opened. If necessary, the digestates are then filtered through filter paper and diluted to 55 mL. The samples are now ready for analysis. The sample results must be corrected by a factor of 1.1 in order to report final concentration values based on an initial volume of 50 mL. Concentrations so determined shall be reported as "total".

10.1.4 Soil/Sediment Sample Preparation

10.1.4.1 Preparation Method/Code (HS1) (USEPA Method 200.7, December 1982)

10.1.4.1.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 1.5 g portion of sample and transfer to a beaker.

10.1.4.1.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C on hot plate or block digester, and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel.

10.1.4.1.3 After the second reflux step has been completed and the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the heat source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

10.1.4.1.4 Add 5 mL of 1:1 HCl and 10 mL of reagent water, return the covered heating vessel to the heat source, and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with reagent water.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

The sample is now ready for analysis.

10.1.4.2 Preparation Method/Code (HS2) (USEPA SW-846 Method 3050B)

10.1.4.2.1 Mix the sample thoroughly to achieve homogeneity. For each digestion procedure, weigh (to the nearest 0.01 g) a 1.0 to 2.0 g portion of sample and transfer to a beaker.

10.1.4.2.2 Add 10 mL of 1:1 nitric acid (HNO_3), mix the slurry, and cover with a watch glass. Heat the sample to 92-95°C on hot plate, block digester, or equivalent heating source, and reflux for 10 minutes without boiling. Allow the sample to cool, add 5 mL of concentrated HNO_3, replace the watch glass, as appropriate, and reflux for 30 minutes. Do not allow the volume to be reduced to less than 5 mL while maintaining a covering of solution over the bottom of the heating vessel. Add an additional 5 mL of concentrated HNO_3 and reflux. Repeat this step until sample oxidation is complete (no brown fumes generated).

10.1.4.2.3 After the reflux steps have been completed and the sample has cooled, add 2 mL of reagent water and 3 mL of 30% hydrogen peroxide (H_2O_2). Return the heating vessel to the heat source for warming to start the peroxide reaction. Care must be taken to ensure that losses do not occur due to excessively vigorous effervescence. Heat until effervescence subsides, and cool the heating vessel.

10.1.4.2.4 Continue to add 30% H_2O_2 in 1 mL aliquots with warming until the effervescence is minimal or until the general sample appearance is unchanged.

NOTE: Do not add more than a total of 10 mL 30% H_2O_2.

10.1.4.2.5 Add 10 mL of concentrated HCl and return the covered heating vessel to the heat source and heat for an additional 10 minutes. After cooling, filter through Whatman No. 42 filter paper (or equivalent) and dilute to 100 mL with reagent water.

NOTE: In place of filtering, the sample (after dilution and mixing) may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

The sample is now ready for analysis.

10.1.4.3 Preparation Method/Code (MS1) (USEPA SW-846 Method 3051)

10.1.4.3.1 Add a representative 0.50 g (±0.01 g) of sample to the PTFE PFA vessel.

10.1.4.3.2 Add 10 mL of concentrated nitric acid. If a vigorous reaction occurs, allow the reaction to stop before capping the vessel.

10.1.4.3.3 Cap the vessel, then tighten using constant torque to 12 ft/lbs, according to the manufacturer's direction.

10.1.4.3.4 Connect the sample vessel to the overflow vessel using PTFE PFA tubing.

10.1.4.3.5 Weigh the vessel assembly to the nearest 0.01 g.

10.1.4.3.6 Place sample vessels in groups of 2 sample vessels or 6 sample vessels in the carousel, evenly spaced around its periphery in the microwave unit. If fewer than the recommended number of samples are to be digested (i.e., 3 samples plus 1 blank) then the remaining vessels must be filled with 10 mL of nitric acid to achieve the full complement of vessels.

10.1.4.3.7 Each sample vessel must be attached to a clean, double-ported vessel to collect any sample expelled from the sample vessel in the event of over pressurization. Assembly of the vessels into the carousel may be done inside or outside the microwave. Connect the overflow vessel to the center well of the oven.

10.1.4.3.8 The PB must have 0.5 mL of reagent water and the same amount (10 mL) of acid that is added to the samples. The PB must later be diluted to 50 mL in the same manner as the samples.

10.1.4.3.9 Irradiate the 2 sample vessel group at 344 watts for 10 minutes, or the 6-sample vessel group at 574 watts for 10 minutes.

10.1.4.3.10 This program brings the samples to 175°C in 5.5 minutes; the temperature remains between 170-180°C for the balance of the 10 minute irradiation period. The pressure should peak at less than 6 atmospheres (atm) for most samples. The pressure may exceed these limits in the case of high concentrations of carbonate or organic compounds. In these cases, the pressure will be limited by the relief pressure of the vessel to 7.5 (±0.7 atm).

10.1.4.3.11 Allow the vessels to cool for a minimum of 5 minutes before removing them from the microwave unit, with exhaust fan on. Allow the vessels to cool to room temperature before opening. The vessels must be carefully vented and uncapped in a fume hood.

10.1.4.3.12 Weigh each vessel assembly. If the weight of acid plus the sample has decreased by more than 10% from the original weight, discard the digests. Determine the reason for the loss. Losses typically are attributed to use of digestion time longer than ten minutes, using too large of a sample, or having improper heating conditions. Once the source of the losses has been corrected, prepare a new set of samples for digestion.

10.1.4.3.13 Sample Filtration: Shake the sample well to mix in any condensate within the digestion vessel before being opened.

Filter the digestion vessel into a 50 mL glass volumetric flask through filter paper. Rinse the sample digestion vessel, cap, connecting tube, and (if venting occurred) the overflow vessel into the 50 mL glass flask. Dilute to 50 mL. The samples are now ready for analysis. Concentrations so determined shall be reported as "total".

10.1.5 Non-Prepared Samples

10.1.5.1 Preparation Method/Code (NP1)

10.1.5.1.1 This code shall be used to report samples that are not digested prior to analysis (e.g., dissolved metal samples that the Contractor was instructed not to digest).

10.1.5.1.2 This Preparation Method/Code shall also be used to report the non-prepared Method Detection Limit (MDL). The concentration of this MDL shall be used to determine the appropriate concentration qualifier for the results of non-prepared samples and instrument Quality Control (QC) analyses.

10.2 Microwave Digestion Cleaning Procedure

10.2.1 Initial Cleaning of the PTFE PFA Digestion Vessels

10.2.1.1 Prior to first use - new vessels must be annealed before they are used. A pretreatment/cleaning procedure must be followed. This procedure calls for heating the vessels for 96 hours at 200°C. The vessels must be disassembled during annealing and the sealing surfaces (the top of the vessel or its rim) must not be used to support the vessel during annealing.

10.2.1.2 Rinse in reagent water.

10.2.1.3 Immerse in 1:1 HCl for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

10.2.1.4 Rinse in reagent water.

10.2.1.5 Immerse in 1:1 HNO_3 for a minimum of 3 hours after the cleaning bath has reached a temperature just below boiling.

10.2.1.6 The vessels are then rinsed with copious amounts of reagent water prior to use for any analyses under this contract.

10.2.2 Cleaning Procedure between Sample Digestions

10.2.2.1 Wash entire vessel in hot water using laboratory-grade non-phosphate detergent.

10.2.2.2 Rinse with 1:1 nitric acid.

10.2.2.3 Rinse 3 times with reagent water.

10.3 Sample Analysis

10.3.1 Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become thermally stable before beginning. This usually requires at least 30 minutes of operation prior to calibration.

10.3.2 Initiate appropriate operating configuration of computer.

10.3.3 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using mixed calibration standard solutions such as those described in Section 7.2.4.5.1.

10.3.4 A minimum of two replicate exposures is required for standardization and all QC and sample analyses. The average result of the multiple exposures for the standardization and all QC and sample analyses shall be used.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous Sample Calculation

The concentrations determined in the digestate are to be reported in units of microgram per Liter (µg/L):

EQ. 2 Aqueous Sample Concentration

$$\text{Concentration (µg/L)} = C \times \frac{V_f}{V_i} \times DF$$

WHERE,
- C = Instrument value in µg/L
- V_f = Final digestion volume (mL)
- V_i = Initial digestion volume (mL)
- DF = Dilution Factor

11.2 Soil Sample Calculation

The concentrations determined in the digestate are to be reported on the basis of the dry weight of the sample, in units of milligrams per kilogram (mg/kg):

EQ. 3 Soil Sample Concentration

$$\text{Concentration (dry wt.) (mg/kg)} = \frac{C \times V}{W \times S} \times DF$$

WHERE,
- C = Concentration (mg/L)
- V = Final sample volume in Liters (L)
- W = Wet sample weight (kg)
- S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
- DF = Dilution Factor

11.3 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, substitute the value of the MDL (µg/L) or CRQL (µg/L) into the "C" term in Equation 2 above.

Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

EQ. 4 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{V_R}{V_M} \times \frac{1}{S} \times DF$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	Minimum method required wet sample weight (g)
W_R	=	Reported wet sample weight (g)
V_M	=	Method required final sample volume (mL)
V_R	=	Reported final sample volume (mL)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
DF	=	Sample Dilution Factor

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. If measurements exceed the control limits of 90% (low) and 110% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. If the deviation of the CCV is greater than the control limits specified of 90% (low) and 110% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and the re-analysis of preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed for the analytes affected. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same acid matrix as the calibration standards, and analyzed at the beginning (immediately following the ICV/ICB) and end of each sample analysis run, immediately preceding the Interference Check Sample (ICS) analyses. In addition, the Contractor shall analyze the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. These analyses of the CRI sample shall be immediately followed by the ICS analyses. [That is, the analytical run sequence shall be CRI, ICS Solution A (ICSA), ICS Solution AB (ICSAB), CCV and Continuing Calibration Blank (CCB), in that order].

12.3.2 The CRI shall be run for every wavelength used for analysis, except those for Al, Ba, Ca, Fe, Mg, Na, and K. Information regarding the CRI shall be reported on Form IIB-IN.

12.3.3 If the percent recovery of the CRI falls outside the control limits of 70-130% (50-150% for antimony, lead, and thallium) for one or more analytes, the CRI shall be re-analyzed immediately for those analytes only. If the results of the re-analysis for those analytes fall within the control limits, no further corrective action is required. If the results of the re-analysis for those analytes do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the Preparation Blank is used to monitor for possible contamination.

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[1]As defined in Exhibit G, CRI is an analytical sample.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acids and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank shall be performed for the elements affected.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If any analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC) for that analyte. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated with the blank, shall be redigested and re-analyzed with appropriate new QC.

12.4.2.4.4 The values for the PB shall be reported on Form III-IN.

12.5 Interference Check Sample (ICS)

12.5.1 The ICS is prepared by the analyst or obtained from USEPA, if available.

[2]A group of samples prepared at the same time.

12.5.2 To verify interelement and background correction factors, the Contractor shall analyze and report the results for the ICS, for all elements on the Target Analyte List (TAL) and for all interferents (target and non-target), at the beginning and end of each analysis run, but not before the ICV. In addition, the Contractor shall analyze and report the results for the ICS at a frequency of not less than once per 20 analytical samples[3] per analysis run. These analyses of the ICS shall be immediately followed by the analysis of a CCV/CCB pair. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to the instructions supplied with the ICS. The Contractor shall not dilute the ICS more than is necessary to meet the linear range values of the instrument.

12.5.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.5.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit of ±2 times the CRQL of the analyte's true value or ±20% of the analyte's true value, whichever is greater (the true value shall be zero unless otherwise stated) in the ICSA. For example, if the analysis result(s) for Arsenic (CRQL = 10 µg/L, ICSA true value = 0 µg/L) in the ICSA analysis during the run is 19 µg/L, then the analytical result for Arsenic falls within the ±2 times the CRQL window for Arsenic in the ICSA. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSA shall be performed. For analytes with CRQLs less than 5000 µg/L, the ICSA results shall be reported from an undiluted sample analysis.

12.5.5 Results for the ICS Solution AB (ICSAB) during the analytical runs shall fall within the control limit of ±2 times the CRQL of the true value or ±20% of the true value, whichever is greater, for the analytes included in the ICSAB. If the analytical results of the ICSA do not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSAB shall be performed.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.5.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for the previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Table 1 - Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS). The mean value and standard deviation shall be established by

[3]As defined in Exhibit G, ICSA and ICSAB are analytical samples.

initially analyzing the Check Samples at least five times repetitively for each parameter on Form IVA-IN. Results shall fall within the control limit of ±2 times the CRQL of the established mean value or ±20% of the established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data. Results from the ICS analyses shall be reported on Form IVA-IN for all Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) analytes.

12.6 Spike Sample Analysis

12.6.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. If a digestion is performed, the spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4]

12.6.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.7). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.6.3 The analyte spike shall be added in the amount given in Table 2 - Spiking Levels for Spike Sample Analysis, for each element analyzed.

NOTE: See Table 2 footnotes for concentration levels and applications.

12.6.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample shall be flagged with the letter "N" on Forms IA/IB-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.6.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those elements that do not meet the specified criteria (exception: Ag). Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike analysis shall be used for the post-digestion spike analysis. Spike the unspiked aliquot of the sample at two times the indigenous level or two times the CRQL, whichever is greater. Results of the post-digestion spike shall be reported on Form VB-IN.

12.6.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

[4]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

EQ. 5 Spike Percent Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.6.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.6.8 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.7 Duplicate Sample Analysis

12.7.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[5] Duplicates cannot be averaged for reporting on Form IA-IN.

12.7.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each component is calculated as follows:

EQ. 6 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.7.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.7.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the

[5]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids, (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA/IB-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each element. Specific control limits for each element will be added to Form VI-IN at a later date based on these precision results.

12.8 Laboratory Control Sample (LCS) Analysis

12.8.1 Water/aqueous and solid LCS shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for the EPA samples received.

12.8.1.1 The aqueous LCS solution (LCSW) shall be obtained from USEPA [if unavailable, the ICV solution(s) may be used]. One LCSW shall be prepared and analyzed for every group of aqueous samples in a SDG, or for each batch of aqueous samples digested, whichever is more frequent.

12.8.1.2 The USEPA provided solid LCS (LCSS) shall be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check Samples or other certified materials may be used. The control limits for these materials and samples must be documented. One LCSS shall be prepared and analyzed for every group of solid samples in a SDG, or for each batch of samples digested, whichever is more frequent.

12.8.2 All LCS and percent recovery results shall be reported on Form VII-IN. If the percent recovery for the LCSW falls outside the control limits of 80-120% (exception: Ag and Sb), the analyses shall be terminated, the problem corrected, and the samples associated with that LCSW redigested and re-analyzed with appropriate new QC.

12.8.3 If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS redigested and re-analyzed with appropriate new QC.

12.9 ICP-AES Serial Dilution Analysis

12.9.1 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP-AES serial dilution analysis. The ICP-AES serial dilution analysis shall be performed on a sample from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG, whichever is more frequent. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.9.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution

analysis for one or more analytes is not within a control limit of 10%, a chemical or physical interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E" on Form VIII-IN and Forms IA/IB-IN.

12.9.3 The percent differences for each component are calculated as follows:

EQ. 7 Serial Dilution Percent Differences

$$\% \text{ Difference} = \frac{|I - S|}{I} \times 100$$

WHERE, I = Initial Sample Result (Instrument reading)

S = Serial Dilution Result (Instrument reading x5)

12.9.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within contract criteria, flag all the samples of the same matrix in the SDG. Serial dilution results and "E" flags shall be reported on Form VIII-IN.

12.10 Method Detection Limit (MDL) Determination

12.10.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for non-prepared analyses (Preparation Method/Code "NP1"), each digestion procedure and instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.10.1.1 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze the non-prepared MDL samples on each instrument used.

12.10.1.2 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.10.1.3 The concentration of the non-prepared MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of non-prepared samples and instrument QC analyses.

12.10.1.4 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.10.1.5 The MDL results shall be reported on Form IX-IN.

12.11 Interelement Corrections

12.11.1 Before any field samples are analyzed under this contract, the interelement correction factors shall be determined prior to the start of contract analyses and at least quarterly thereafter. Correction factors for spectral interference due to Al, Ca, Fe, and Mg shall be determined for all ICP-AES instruments at all wavelengths

used for each analyte reported by ICP-AES. Interelement correction factors shall also be reported for any other elements (including those on the TAL) that have been determined to interfere with the requested target analyte(s).

NOTE: Depending on sample matrix and interferences, it may be necessary to analyze interelement correction factors at a frequency greater than quarterly and/or at multiple concentrations comparable to the sample interferent levels.

12.11.2 If the instrument was adjusted in any way that may affect the ICP-AES interelement correction factors, the factors shall be redetermined and the results submitted for use. In addition, all data used for the determination of the interelement correction factors shall be available to the USEPA during an on-site laboratory evaluation. Results from interelement correction factors determination shall be reported on Form XA-IN and Form XB-IN for all ICP-AES analytes.

12.12 Linear Range Standard (LRS)

12.12.1 Before any field samples are analyzed under this contract, the linear ranges shall be determined and reported prior to the start of contract analyses, and at least quarterly thereafter by the analysis of a linear range verification check standard, for each element on Form XI-IN. The standard shall be analyzed during a routine analytical run performed under this contract. The analytically determined concentration of this standard shall be within 5% of the true value. This concentration is the upper limit of the ICP-AES linear range beyond which results cannot be reported under this contract without dilution of the analytical sample.

12.13 Example Analytical Sequence for ICP-AES

S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
7 samples
CRI
ICSA
ICSAB
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 200.7. December 1982.

16.2 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3050B. Third Edition, Update III. December 1996.

16.3 American Society for Testing and Materials. Standard Practice for Sample Digestion Using Closed Vessel Microwave Heating Technique for the Determination of Total Recoverable Metals in Water. D4309-91. October 1991.

16.4 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

16.5 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3015. Third Edition, Update II. September 1994.

16.6 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 3051. Third Edition, Update II. September 1994.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

TABLE 1: Interferent and Analyte Elemental Concentrations Used for ICP-AES Interference Check Sample (ICS)

Analytes	(mg/L)	Interferents	(mg/L)
Ag	0.2	Al	250
As	0.1	Ca	250
Ba	0.5	Fe	100
Be	0.5	Mg	250
Cd	1.0		
Co	0.5		
Cr	0.5		
Cu	0.5		
Mn	0.5		
Ni	1.0		
Pb	0.05		
Sb	0.6		
Se	0.05		
Tl	0.1		
V	0.5		
Zn	1.0		

NOTE: ICS Solution A (ICSA) contains the interferents at the indicated concentrations. The ICSA may be analyzed at twice the concentration indicated when interferences are present at higher concentrations in the sample. ICS Solution AB (ICSAB) contains all of the analytes and interferents listed above at the indicated concentrations.

TABLE 2: Spiking Levels for Spike Sample Analysis

Element	Water (µg/L)	Soil[(1)] (mg/kg)	Element	Water (µg/L)	Soil[(1)] (mg/kg)
Aluminum	2,000	*	Magnesium	*	*
Antimony	100	20	Manganese	500	100
Arsenic	40	8	Nickel	500	100
Barium	2,000	400	Potassium	*	*
Beryllium	50	10	Selenium	50	10
Cadmium	50	10	Silver	50	10
Calcium	*	*	Sodium	*	*
Chromium	200	40	Thallium	50	10
Cobalt	500	100	Vanadium	500	100
Copper	250	50	Zinc	500	100
Iron	1,000	*			
Lead	20	4			

[*]No spike required. NOTE: Elements without spike levels, and not designated with an asterisk, shall be spiked at appropriate levels.

[1]The levels shown indicate concentrations in the spike sample when the wet weight of 1 gram of sample is taken for analysis. Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values. Appropriate adjustment shall be made for microwave digestion procedures where 0.5 grams of sample or 50 mL (45 mL of sample plus 5 mL of acid) or 55 mL (50 mL of sample plus 5 mL of acid) of aqueous sample are required for analysis.

EQ. 8 Spiking Level Adjustment

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final volume (L)}}{\text{sample weight (g)}}$$

EXHIBIT D - PART B

ANALYTICAL METHODS FOR INDUCTIVELY COUPLED PLASMA - MASS SPECTROMETRY

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Exhibit D - Analytical Methods for ICP-MS

Table of Contents

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1.0 SCOPE AND APPLICATION

This method provides procedures for the use of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) to determine the concentration of dissolved and total recoverable elements in water/aqueous samples taken from hazardous waste sites. This method is applicable to all metals in the Target Analyte List (TAL) for ICP-MS in Exhibit C.

2.0 SUMMARY OF METHOD

This method describes the multi-element determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). Sample material in solution is introduced by nebulization into a radio frequency plasma where energy transfer processes cause desolvation, atomization, and ionization. The ions are extracted from the plasma through a differentially pumped vacuum interface and separated on the basis of their mass-to-charge ratio. The separated ions are detected and the ion information processed by a data handling system. Interferences related to the technique must be recognized and corrected. Such corrections may include compensation for isobaric elemental interferences and interferences from polyatomic ions derived from plasma gas, reagents, or sample matrix. Instrumental drift, as well as suppressions or enhancements of instrument response, must be corrected for the use of internal standards.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Several types of interferences may cause inaccuracies in the determination of trace elements by Inductively Coupled Plasma - Mass Spectrometry (ICP-MS). To prevent this, appropriate steps must be taken in all analyses to ensure that potential interferences are taken into account. Possible interferences are in Sections 4.1 through 4.5.

4.1 Isobaric Elemental Interferences

Isobaric Elemental Interferences are caused by isotopes of different elements which form singly or doubly charged ions of the same nominal mass-to-charge ratio, and which cannot be resolved by the mass spectrometer. All elements determined by this method have, at minimum, one isotope free of isobaric elemental interference. Of the analytical isotopes recommended for use with this method, only selenium-82 (krypton) has an isobaric elemental interference. If alternative analytical isotopes having higher natural abundances are selected, in order to achieve greater sensitivity, an isobaric interference may occur. All data obtained under such conditions must be corrected by measuring the signal from another isotope of the interfering element and subtracting the appropriate signal ratio from the isotope of interest. A record of this correction process should be included with the report of the data. It should be noted that such corrections will only be as accurate as the accuracy of the isotope ratio used in the elemental equation for data calculations. Relevant isotope ratios should be established prior to the application of any corrections.

4.2 Abundance Sensitivity

Abundance Sensitivity is a property defining the degree to which the wings of a mass peak contribute to adjacent masses. The abundance sensitivity is affected by ion energy and mass filter operating pressure. Wing overlap interferences may result when a small ion peak is being measured adjacent to a large one. The potential for these interferences should be recognized and the spectrometer resolution should be adjusted to minimize.

4.3 Isobaric Polyatomic Ion Interferences

These are caused by ions consisting of more than one atom which have the same nominal mass-to-charge ratio as the isotope of interest, and which cannot be resolved by the mass spectrometer. These ions are commonly formed in the plasma or interface system from support gases or sample components. Most of the common interferences have been identified and are listed in Table 1 - Isobaric Molecular-Ion Interferences, with the target analytes affected. Such interferences must be recognized, and when they cannot be avoided by the selection of alternative analytical isotopes, appropriate corrections must be made to the data. Equations for the correction of data should be established at the time of the analytical run sequence, since the polyatomic ion interferences will be highly dependent on the sample matrix and chosen instrument conditions.

4.4 Physical Interferences

These are associated with the physical processes which govern the transport of the sample into the plasma, sample conversion processes in the plasma, and the transmission of ions through the plasma-mass spectrometer interface. These interferences may result in differences between instrument responses for the sample and the calibration standards. Physical interferences may occur in the transfer of solution to the nebulizer (e.g., viscosity effects), at the point of aerosol formation and transport to the plasma (e.g., surface tension), or during

the excitation and ionization processes within the plasma itself. High levels of dissolved solids in the sample may contribute to deposits of material on the extraction and/or skimmer cones. Deposits can reduce the effective diameter of the orifices and therefore ion transmission. Dissolved solid levels not exceeding 0.2% (w/v) have been recommended to reduce such effects. Internal standardization may be effectively used to compensate for many physical interference effects. Internal standards ideally should have similar analytical behavior to the elements being determined.

4.5 Memory Interferences

Memory Interferences result when isotopes of elements in a previous sample contribute to the signals measured in a new sample. Memory effects, or carryover, can result from sample deposition on the sampler and skimmer cones, as well as from the buildup of sample material in the plasma torch and spray chamber. The site where these effects occur is dependent on the element and can be minimized by flushing the system with a rinse blank between samples (see Section 7.3.3). The possibility of memory interferences should be recognized within an analytical run and suitable rinse times should be used to reduce them. The rinse times necessary for a particular element should be estimated prior to analysis. This may be achieved by aspirating a standard, containing the elements corresponding to ten times the upper end of the linear range for a normal sample analysis period, followed by analysis of the rinse blank at designated intervals. The length of time required to reduce analyte signals to within a factor of ten of the Method Detection Limit (MDL) should be noted. Memory interferences may also be assessed within an analytical run by using a minimum of three replicate integrations for data acquisition. If the integrated signal values drop consecutively, the analyst should be alerted to the possibility of a memory effect, and should examine the analyte concentration in the previous sample to identify if it was high. If a memory interference is suspected, the sample should be re-analyzed after a long rinse period.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Glassware/Labware

6.1.1 250 milliliter (mL) beaker or other appropriate vessel (glass or plastic)

6.1.2 Watch glasses (glass or plastic)

6.1.3 Funnels

6.1.4 Graduated cylinders

6.1.5 Various volumetric flasks (Type A)

6.1.6 Thermometer that covers range of 0-200°C

6.1.7 Whatman No. 42 filter paper or equivalent

6.1.8 Hot plate, block digester, or other heating source capable of maintaining 92-95°C.

6.1.9 Balances - Analytical Balance, 300 gram (g) capacity, and minimum ±0.1 milligram (mg).

6.2 Inductively Coupled Plasma Mass Spectrometer (ICP-MS) consisting of:

- An instrument capable of scanning the mass range 5-250 atomic mass unit (amu) with a minimum resolution capability of 1 amu peak width at 5% peak height and either a conventional or extended dynamic range detector.
- A radio-frequency generator compliant with Federal Communications Commission (FCC) regulations.
- A high purity (99.99%) argon gas supply.
- A variable speed peristaltic pump to deliver sample solution to the nebulizer.
- A mass-flow controller on the nebulizer gas supply is required.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

Reagents may contain elemental impurities that might affect the integrity of analytical data. Owing to the high sensitivity of Inductively Coupled Plasma - Mass Spectrometry (ICP-MS), high-purity reagents should be used whenever possible. Suitable acids are available from a number of manufacturers or may be prepared by sub-boiling distillation. Nitric acid is preferred for ICP-MS in order to minimize polyatomic ion interferences. Several polyatomic ion interferences result when hydrochloric acid (HCl) is used, however, it should be noted that HCl is required to maintain stability in solutions containing antimony and silver. When HCl is used, corrections for the chloride polyatomic ion interferences must be applied to all data.

7.1.1 Reagent Water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Nitric Acid - Concentrated (specific gravity 1.41).

7.1.3 Nitric acid (1+1) - Add 500 milliliters (mL) conc. HNO_3 to 400 mL of reagent water and dilute to 1 Liter (L).

7.1.4 Nitric acid (1+9) - Add 100 mL conc. nitric acid to 400 mL of reagent water and dilute to 1 L.

7.1.5 Hydrochloric acid - Concentrated (specific gravity 1.19).

7.1.6 Hydrochloric acid (1+1) - Add 500 mL conc. HCl to 400 mL of reagent water and dilute to 1 L.

7.1.7 Hydrochloric acid (HCl) (1+4) - Add 200 mL conc. HCl to 400 mL reagent water and dilute to 1 L.

7.1.8 Ammonium hydroxide - Concentrated (specific gravity 0.902).

7.1.9 Tartaric acid - (CASRN 87-69-4).

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer’s certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock standard solutions may be purchased from a reputable commercial source or prepared from reagent grade chemicals or metals (99.99-99.999% pure). All salts should be dried for 1 hour at 105°C unless otherwise specified. Stock solutions should be stored in Fluorinated Ethylene Propylene (FEP) fluorocarbon bottles. Note that some metals, particularly those which form surface oxides, require cleaning prior to being weighed. This may be achieved by pickling the surface of the metal in acid. An amount in excess of the desired weight should be pickled

repeatedly, rinsed with water, dried and weighed until the desired weight is achieved.

7.2.2.2 Aluminum solution, stock [1 mL = 1000 micrograms (µg) Al] - Pickle aluminum metal in warm (1+1) HCl to an exact weight of 0.100 g. Dissolve in 10 mL conc. HCl and 2 mL conc. nitric acid, heating to effect solution. Continue heating until the volume is reduced to 4 mL. Cool and add 4 mLs of reagent water. Heat until volume is reduced to 2 mL. Cool and dilute to 100 mL with reagent water.

7.2.2.3 Antimony solution, stock (1 mL = 1000 µg Sb) - Dissolve 0.100 g antimony powder in 2 mL (1+1) nitric acid and 0.5 mL conc. HCl, heating to effect solution. Cool, add 20 mL reagent water and 0.15 g tartaric acid. Warm the solution to dissolve the white precipitate. Cool and dilute to 100 mL with reagent water.

7.2.2.4 Arsenic solution, stock (1 mL = 1000 µg As) - Dissolve 0.1320 g As_2O_3 in a mixture of 50 mL reagent water and 1 mL conc. ammonium hydroxide. Heat gently to dissolve. Cool and acidify solution with 2 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.5 Barium solution, stock (1 mL = 1000 µg Ba) - Dissolve 0.1437 g $BaCO_3$ in a solution mixture of 10 mL reagent water and 2 mL conc. nitric acid. Heat and stir to effect solution and degassing. Dilute to 100 mL with reagent water.

7.2.2.6 Beryllium solution, stock (1 mL = 1000 µg Be) - Dissolve 1.965 g $BeSO_4 \bullet 4H_2O$ (DO NOT DRY) in 50 mL reagent water. Add 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.7 Bismuth solution, stock (1 mL = 1000 µg Bi) - Dissolve 0.1115 g Bi_2O_3 in 5 mL conc. nitric acid. Heat to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.8 Cadmium solution, stock (1 mL = 1000 µg Cd) - Pickle cadmium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.9 Chromium solution, stock (1 mL = 1000 µg Cr) - Dissolve 0.1923 g CrO_3 in a solution mixture of 10 mL reagent water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.10 Cobalt solution, stock (1 mL = 1000 µg Co) - Pickle cobalt metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.11 Copper solution, stock (1 mL = 1000 µg Cu) - Pickle copper metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.12 Indium solution, stock (1 mL = 1000 µg In) - Pickle indium metal in (1+1) nitric acid to an exact weight of 0.100 g. Dissolve in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.13 Lead solution, stock (1 mL = 1000 µg Pb) - Dissolve 0.1599 g $PbNO_3$ in 5 mL (1+1) nitric acid. Dilute to 100 mL with reagent water.

7.2.2.14 Magnesium solution, stock (1 mL = 1000 µg Mg) - Dissolve 0.1658 g MgO in 10 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.15 Manganese solution, stock (1 mL = 1000 µg Mn) - Pickle manganese flake in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.16 Nickel solution, stock (1 mL = 1000 µg Ni) - Dissolve 0.100 g nickel powder in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.17 Scandium solution, stock (1 mL = 1000 µg Sc) - Dissolve 0.1534 Sc_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.18 Selenium solution, stock (1 mL = 1000 µg Se) - Dissolve 0.1405 g SeO_2 in 20 mL reagent water and dilute to 100 mL with reagent water.

7.2.2.19 Silver solution, stock (1 mL = 1000 µg Ag) - Dissolve 0.100 g silver metal in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water. Protect from the light.

7.2.2.20 Terbium solution, stock (1 mL = 1000 µg Tb) - Dissolve 0.1176 g Tb_4O_7 in 5 mL conc. nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.21 Thallium solution, stock (1 mL = 1000 µg Tl) - Dissolve 0.1303 g $TlNO_3$ in a solution mixture of 10 mL reagent water and 1 mL conc. nitric acid. Dilute to 100 mL with reagent water.

7.2.2.22 Vanadium solution, stock (1 mL = 1000 µg V) - Pickle vanadium metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.23 Yttrium solution, stock (1 mL = 1000 µg Y) - Dissolve 0.1270 g Y_2O_3 in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.2.24 Zinc solution, stock (1 mL = 1000 µg Zn) - Pickle zinc metal in (1+9) nitric acid to an exact weight of 0.100 g. Dissolve in 5 mL (1+1) nitric acid, heating to effect solution. Cool and dilute to 100 mL with reagent water.

7.2.3 Secondary Dilution Standards

Prepare mixed secondary dilution standard solutions by diluting the appropriate volumes of stock standards with acidified reagent water to obtain the final volume. Originating stock standards should be checked for the presence of impurities which might influence the accuracy of the standard. Freshly prepared standards should be transferred to acid-cleaned, not previously used, FEP fluorocarbon bottles for storage and monitored periodically for stability. Mixed secondary dilution standard solutions may be purchased. The purchased standards shall meet the requirements in Section 7.2.1.

7.2.4 Working Standards

7.2.4.1 Mixed Calibration Standard Solutions

Care must be taken in the preparation of mixed calibration standards to ensure that the elements are compatible and stable. Fresh calibration standards should be prepared from mixed standard solutions every two weeks or as needed. Dilute the mixed standards to levels appropriate to the operating range of the instrument using reagent water containing 1% (v/v) nitric acid. The element concentrations in the calibration standards should be sufficiently high to produce good measurement precision and to accurately define the slope of the response curve. If the direct addition procedure is being used, add internal standards.

7.2.4.2 Internal Standard Solution

Prepare mixed standard by diluting 10 mL each of the chosen element's stock standards to 100 mL with reagent water. Use this solution for additions to blanks, calibration standards, and samples, or dilute by an appropriate amount using 1% (v/v) nitric acid if the internal standards are being added by a peristaltic pump.

7.2.4.3 Tuning Solution

This solution is used for instrument tuning and mass calibration prior to analysis. Prepare mixed standard by diluting beryllium, magnesium, cobalt, indium, and lead stock standards to 100 µg/L with 1% (v/v) nitric acid. Do not add internal standard to this solution.

7.2.4.4 Interference Check Sample (ICS)

The ICS consists of two solutions: Solution A (ICSA) and Solution AB (ICSAB). ICSA consists of the interferents and ICSAB consists of the analytes mixed with the interferents. If the direct addition procedure is being used, add internal standards.

7.2.4.4.1 Solution A - Contains 100 milligrams per Liter (mg/L) of aluminum, calcium, iron, magnesium, potassium, sodium, phosphorus (as orthophosphate), sulfur (as sulfate), 200 mg/L carbon, 1000 mg/L chloride, and 2 mg/L molybdenum and titanium.

7.2.4.4.2 Solution AB - Contains all of the elements in Solution A plus all target analytes at a concentration of 20 µg/L.

7.2.4.5 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentrations of the analytes in the CRI shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.4.6 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.3 Blanks

Three types of blanks are required for this method. A calibration blank is used to establish the analytical calibration curve, the Preparation Blank (PB) (see Section 12.5.2) is used to assess possible contamination

from the sample preparation procedure and to assess spectral background, and the rinse blank is used to flush the instrument between samples in order to reduce memory interferences.

7.3.1 Calibration Blank - Consists of 1% (v/v) nitric acid in reagent water. If the direct addition procedure is being used, add internal standards.

7.3.2 Preparation Blank - Must contain all the reagents in the same volumes as used in preparing the samples. The PB must be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

7.3.3 Rinse Blank - Consists of 2% (v/v) nitric acid in reagent water.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedures for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after the delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Procedure for Sample Digestate Storage

Sample digestates must be stored until 365 days after delivery of a complete, reconciled data package to USEPA.

8.4 Contract Required Holding Time

The maximum holding time for metals is 180 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the differences between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. Instead, the analyst should follow the instructions provided by the manufacturer of the particular instrument. The Method Detection Limit (MDL), precision, linear dynamic range, and interference effects must be investigated and established for each individual element on that particular instrument. All measurements must be within the operational range of the instrument where corrections are valid. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) Instrument Calibration Procedure

9.2.1 Precalibration routine - The following precalibration routine must be completed prior to calibrating the instrument.

Set up the instrument with proper operating parameters established in Section 9.1. The instrument must be allowed to become stable prior to calibration. Conduct any necessary mass calibration and resolution routines to bring peak width within the manufacturer's specifications and adjust mass calibration to within 0.1 amu over the range of 6 to 210 amu.

Demonstrate instrument stability and precision by analyzing the tuning solution a minimum of five times consecutively. This may be carried out as five separate analyses or as a single analysis with at least five integrations. The percent relative standard deviation of the absolute signals for all analytes in the tuning solution must be less than 5%.

9.2.2 Internal Standardization

Internal standardization must be used in all analyses (except the tuning solution) to correct the instrument drift and physical interferences. A list of acceptable internal standards is provided in Table 4 - Internal Standards. For full range mass scans, a minimum of five internal standards shall be used. The masses of the internal standards shall bracket the masses of the analyte. The internal standards selected for a run must be consistent throughout the entire run. Internal standards shall be present in all samples, standards, and blanks (except the tuning solution) at identical levels. This may be achieved by directly adding an aliquot of the internal standards solution to each sample, standard, and blank, or by mixing with the sample solution prior to nebulization using a second channel of the peristaltic pump and mixing coil. The concentration of the internal standard should be sufficiently high for good precision and to minimize the possibility of correction errors if the internal standard is naturally present in the sample. Depending on the sensitivity of the instrument, a concentration range of 20 µg/L to 200 µg/L of each internal standard is recommended. Internal standards should be added to samples, standards, and blanks in a similar manner, in order for dilution effects to be disregarded.

9.2.3 Calibration

Instruments shall be calibrated daily, once every 24 hours, or each time the instrument is set up. The instrument standardization date and time shall be included in the raw data. Calibration standards shall be prepared as in Section 7.2.4.1. Calibrate the instrument with at least two standards, one of which must be a blank standard. A minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for instrument calibration and data reporting.

NOTE: Any changes or corrections to the analytical system shall be followed by recalibration.

9.3 Initial Calibration Verification (ICV)

9.3.1 Immediately after each instrument has been calibrated, the accuracy of the initial calibration shall be verified and documented for every analyte by the analysis of the ICV solution(s) for each mass used to report final results.

9.3.2 Only if the ICV solution(s) is(are) not available from USEPA, or where a certified solution of an analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source other than those used in the standards for instrument calibration.

9.3.3 The ICV solution(s) shall be run at each mass used for reporting final results. The values for the ICV shall be reported on Form IIA-IN.

9.4 Continuing Calibration Verification (CCV)

9.4.1 To ensure calibration accuracy during each analysis run, one of the following standards shall be used for the CCV for each mass used for reporting final results for each element, at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported for each mass used for reporting final results for each element at the beginning of the run and after the last analytical sample. The analyte concentrations in the CCV standard(s) shall be different from the concentrations for the ICV and shall be one of the following solutions at or near one-half of the calibration standard:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.4.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations which may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in

time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.4.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.5 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed for each mass used for reporting final results for each element immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results of the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analysis be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analysis will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample and analyze one or more of the phases, separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is(are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Sample Preparation Procedures

10.1.3.1 Preparation Method/Code (HW2)

Shake and transfer a 100 mL aliquot of the sample to a 250 mL heating vessel, add 2 mL (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid (HCl) to the sample. Cover with a ribbed watch glass and heat on either a hot plate, block digester, or equivalent heating source which is adjustable and capable of maintaining a temperature of 92-95°C for 2 hours, or until the sample volume is reduced to about 20 mL (DO NOT BOIL). Cover with a watch glass to prevent additional evaporation and reflux for 30 minutes. Cool sample, transfer to a 50 mL volumetric flask, and adjust sample volume to 50 mL with reagent water. Mix and allow any solids present to settle by gravity overnight or centrifuge (if after settling or centrifuging, the sample contains suspended solids, a portion of the sample may be filtered prior to analysis).

10.1.3.1.1 Prior to analysis, adjust the chloride concentration by pipetting 20 mL of the digestate into a 50 mL volumetric flask and dilute to volume with reagent water and mix. If the direct addition method is being used, add internal standards and mix. The sample is now ready for analysis.

10.1.3.2 Preparation Method/Code (HW3)

Shake sample and transfer 50-100 mL of well-mixed sample to an appropriate polytetrafluoroethylene (PTFE), polypropylene, or polyethylene heating vessel. Add 2 mL of (1+1) nitric acid and 1 mL of (1+1) hydrochloric acid to the vessel. Cover with a ribbed watch glass or similar cover and heat on a hot plate, block digester, or equivalent heating source that is adjustable and capable of maintaining a temperature of 92-95°C until the sample volume has been reduced by half. Cover with a watch glass or similar cover to prevent further evaporation and reflux for an additional 30 minutes. Cool sample and filter to remove insoluble material.

NOTE: In place of filtering, the sample, after dilution and mixing, may be centrifuged or allowed to settle by gravity overnight to remove insoluble material.

Adjust volume to 50-100 mL with reagent water. The sample is now ready for analysis. If volumes less than 100 mL are used, all other reagents shall be reduced appropriately (e.g., if 50 mL is used, reduce reagent volumes by one-half). The final volume of the digestate must equal the initial volume of the sample aliquot.

10.2 Sample Analysis

10.2.1 For every new or unusual matrix, it is highly recommended that a semi-quantitative analysis be carried out to screen for high element concentrations. Information gained from this may be used to prevent potential damage to the detector during sample analysis and to identify elements which may be higher than the linear range. Matrix screening may be carried out by diluting the sample by a factor of 500 and analyzing in semi-quantitative mode. The sample should also be screened for background levels of all elements chosen for use as internal standards in order to prevent bias in the calculation of analytical data.

10.2.2 Initiate instrument operating configuration. Tune and calibrate the instrument for the analytes of interest. Establish instrument software run procedures for quantitative analysis. For all sample analyses, a minimum of three replicate integrations are required for data acquisition. Use the average of the integrations for data reporting.

10.2.3 The rinse blank should be used to flush the system between samples. Allow sufficient time to remove traces of the previous sample or a minimum of one minute. Samples should be aspirated for a sufficient period of time to obtain a stable response prior to the collection of data.

10.2.4 Samples having concentrations higher than the established linear dynamic range should be diluted into range and re-analyzed. The sample should first be analyzed for the trace elements, protecting the detector from the high concentration elements, if necessary, by the selection of appropriate scanning windows. The sample should then be diluted for the determination of the remaining elements. Alternatively, the dynamic range may be adjusted by selecting an alternative isotope of lower natural abundance, provided QC data for that isotope have been established. The dynamic range must not be adjusted by altering instrument conditions to an uncharacterized state.

10.2.5 All masses which might affect data quality must be monitored during the analytical run. At a minimum, those masses prescribed in Table 2 - Mass Choices for Elements that Must Be Monitored During the Analytical Run, must be monitored in the same scan that is used for the collection of the data. This information should be used to correct the data for identified interferences.

10.2.6 During the analysis of samples, the laboratory must comply with the required QC described in Section 12. For the determination of dissolved analytes when the Region has specified that no preparation is required, the Preparation Blank (PB) and Laboratory Control Sample (LCS) are not required.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Recommended Elemental Equations

Elemental expressions recommended for sample data calculations are listed in Table 3 - Recommended Elemental Expressions for Isobaric Interferences. Do not report element concentrations below the determined Method Detection Limit (MDL).

11.2 Data Value Corrections

Data values should be corrected for instrument drift or sample matrix induced interferences by the application of internal standardization. Corrections for characterized spectral interferences should be applied to the data. Chloride interference corrections should be made on all samples, regardless of the addition of hydrochloric acid (HCl), as the chloride ion is a common constituent of environmental samples.

11.3 Multiple Monitored Isotopes

If an element has more than one monitored isotope, examination of the concentration calculated for each isotope or the isotope ratios will provide useful information in detecting a possible spectral interference. Consideration should therefore be given to both primary and secondary isotopes in the evaluation of sample concentration. In some cases, secondary isotopes may be less sensitive or more prone to interferences than the primary recommended isotopes, therefore differences between the results do not necessarily indicate a problem with data calculated for the primary isotopes.

11.4 Prepared Sample Analysis (HW2)

EQ. 1 Prepared Sample Concentration by Method HW2

$$\text{Concentration } (\mu g/L) = C \times \frac{V_f}{V_i} \times \frac{V_f}{20} \times DF$$

WHERE,

- C = Instrument value in µg/L (The average of all replicate integrations).
- V_f = Final digestion volume (50 mL)
- V_i = Initial digestion volume (100 mL)
- DF = Dilution Factor

11.5 Prepared Sample Analysis (HW3)

EQ. 2 Prepared Sample Concentration by Method HW3

$$\text{Concentration (g/L)} = C \times \frac{V_f}{V_i} \times DF$$

WHERE,

- C = Instrument value in µg/L (The average of all replicate integrations).
- V_f = Final digestion volume (mL)
- V_i = Initial digestion volume (mL)
- DF = Dilution Factor

11.6 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted CRQL or adjusted MDL, multiply the value of the CRQL (µg/L) or MDL (µg/L) by the sample dilution factor.

12.0 QUALITY CONTROL (QC)

12.1 Tune Standard

The Tune Standard shall be prepared in the same acid matrix as the calibration standards and analyzed at least 5 times consecutively. Analyses may be carried out as five separate analyses or as a single analysis with at least five integrations. If the mass calibration is not within 0.1 amu over the range of 6 to 210 amu, or the percent Relative Standard Deviation (%RSD)of the absolute signals of the analytes exceeds 5%, the analysis shall be terminated, the problem corrected, and the instrument re-tuned. All sample results reported must be associated with an instrument tune that meets these requirements.

12.2 Initial Calibration Verification (ICV)

The ICV Standard shall be prepared in the same acid matrix as the calibration standards and in accordance with the instructions provided by the supplier. If measurements exceed the control limits of 90% (low) and 110% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.3 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by combining compatible elements at a concentration equivalent to the mid-points of their respective calibration curves. If the deviation of the CCV is greater than the specified control limits of 90% (low) and 110% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed for the elements affected. Information regarding the CCV shall be reported on Form IIA-IN.

12.4 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.4.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same acid matrix as the calibration standards, and analyzed at the beginning (immediately following the ICV/ICB and immediately preceding the Interference Check Sample (ICS) analyses). In addition, the contractor shall analyze the CRI at the end of each sample analysis run and at a frequency of not less than once per 20 analytical samples[1] per analysis run. These subsequent analyses of the CRI shall be immediately followed by CCV/CCB analyses.

12.4.2 The CRI shall be run for every required isotope used for the analysis of all Inductively Coupled Plasma - Mass Spectrometry (ICP-MS) analytes. Information regarding the CRI shall be reported on Form IIB-IN.

12.4.3 If the percent recovery of the CRI falls outside the control limits of 70-130% (50-150% for cobalt, manganese, and zinc) for one or more analytes, the CRI shall be re-analyzed immediately for those analytes only. If the results of the re-analysis for those analytes fall within the control limits, no further corrective action is required. If the results of the re-analysis for those analytes do not fall within the control limits, the analysis shall be terminated, the

[1]As defined in Exhibit G, CRI is an analytical sample.

problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.5 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.5.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acid and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration blank shall be performed for the elements affected.

12.5.2 Preparation Blank (PB)

12.5.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.5.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.5.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.5.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.5.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.5.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of that analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples, associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC) for that analyte. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.5.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL associated

[2]A group of samples prepared at the same time.

with the blank, shall be redigested and re-analyzed with appropriate new QC.

12.5.2.4.4 The values for the PB shall be reported on Form III-IN.

12.6 Interference Check Sample (ICS)

12.6.1 The ICS is prepared by the analyst or obtained from USEPA, if available.

12.6.2 To verify corrections for elemental and polyatomic isobaric interferences, the Contractor shall analyze and report the results for the ICS for all elements on the Target Analyte List (TAL) and analyze for all interferents, at the beginning of each analysis run, but not before the ICV. This analysis of the ICS shall be immediately followed by analysis of a CCV/CCB pair. The ICS solutions shall be obtained from USEPA, if available, and analyzed according to instructions supplied with the ICS. The Contractor shall not dilute the ICS (for the higher concentration elements) more than is necessary to meet the linear range values of the instrument.

12.6.3 The ICS consists of two solutions: Solution A and Solution AB. Solution A consists of the interferents, and Solution AB consists of the analytes mixed with the interferents. An ICS analysis consists of analyzing both solutions consecutively, starting with Solution A.

12.6.4 The analytical results of ICS Solution A (ICSA) shall fall within the control limit of ±3 times the CRQL of the analyte's true value or ±20% of the analyte's true value (the true value shall be zero unless otherwise stated) in the ICSA, whichever is greater. If not, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSA shall be performed. The ICSA results for these analytes shall be reported from an undiluted sample analysis.

12.6.5 Results for the ICS Solution AB (ICSAB) during the analytical runs shall fall within the control limit of ±3 times the CRQL of the true value or ±20% of the true value, whichever is greater, for the analytes included in the ICSAB. If not, the analysis shall be terminated, the problem corrected, the instrument recalibrated, and re-analysis of the analytical samples analyzed since the last compliant ICSAB shall be performed.

NOTE: The control limits and concentrations for the ICSAB are being monitored. These may be adjusted to provide greater control of interferences.

12.6.6 If true values for analytes contained in the ICS are not supplied with the solutions, the mean shall be determined by initially analyzing the ICS at least five times repetitively for the particular analytes. This mean determination shall be made during an analytical run where the results for a previously supplied ICS met all contract specifications. Additionally, the results of this initial mean determination shall be used as the true value for the lifetime of that solution (i.e., until the solution is exhausted). Only if the ICS solutions are not available from USEPA, independent Check Samples shall be prepared with interferent and analyte concentrations at the levels specified in Sections 7.2.4.4.1 and 7.2.4.4.2. The mean value and standard deviation shall be established by initially analyzing the Check Samples at least five times repetitively for each analyte listed on Form IVB-IN. Results shall fall within the control limit of ±3 times the CRQL of the established mean value or ±20% of the

established mean value, whichever is greater. The mean and standard deviation shall be reported in the raw data. Results from the ICS analyses shall be reported on Form IVB-IN for all ICP-MS parameters.

12.7 Spike Sample Analysis

12.7.1 The spike sample analysis is designed to provide information about the effect of sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed for each SDG[3].

12.7.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated "original sample" (see Section 12.8). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.7.3 The analyte spike shall be added in the amount given in Table 5 - Spiking Levels for Spike Sample Analysis, for each element analyzed.

12.7.4 If the spike recovery is not at or within the limits of 75-125%, the data for all samples received and associated with that spike sample and shall be flagged with the letter "N" on Forms IA/IB-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the Spike Added (SA) concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.7.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed four times the spike added, a post-digestion spike shall be performed for those elements that do not meet the specified criteria. Note that if a post-digestion spike analysis is required for an analyte, the same EPA sample that was used for the matrix spike shall be used for the post-digestion spike analysis. Spike an unspiked aliquot of the digestate at two times the indigenous level or two times the CRQL, whichever is greater. Results of the post-digestion spike shall be reported on Form VB-IN.

12.7.6 In the instance where there is more than one spike sample per matrix per SDG, if one spike sample recovery is not within contract criteria, flag all the samples in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 3 Spike Percent Recovery

$$\%\text{Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spike Sample Result

SR = Sample Result

SA = Spike Added

[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.7.7 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.7.8 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.8 Duplicate Sample Analysis

12.8.1 One duplicate sample shall be analyzed for each SDG[4]. Duplicates cannot be averaged for reporting on Form IA-IN.

12.8.2 Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) for each analyte is calculated as follows:

EQ. 4 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S-D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.8.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit equal to the CRQL shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.8.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA/IB-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the methods for each element. Specific control limits for each element may be added to Form VI-IN at a later date based on these precision results.

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

12.9 Laboratory Control Sample (LCS) Analysis

12.9.1 A water/aqueous LCS (LCSW) shall be analyzed for each analyte using the same sample preparations, analytical methods, and Quality Assurance/Quality Control (QA/QC) procedures employed for USEPA samples received.

12.9.2 The LCSW solution must be obtained from USEPA (if unavailable, the ICV solution(s) may be used). One aqueous LCS shall be prepared and analyzed for each group of samples in an SDG, or for each batch of samples digested, whichever is more frequent.

12.9.3 All LCSW and percent recovery results shall be reported on Form VII-IN. If the percent recovery for the LCSW falls outside the control limits of 80-120%, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSW redigested and re-analyzed with appropriate new QC.

12.10 ICP-MS Serial Dilution Analysis

12.10.1 Prior to reporting concentration data for the analyte elements, the Contractor shall analyze and report the results of the ICP-MS serial dilution analysis. The ICP-MS serial dilution analysis shall be performed on a sample from each SDG. Samples identified as field blanks and PE samples shall not be used for serial dilution analysis.

12.10.2 If the analyte concentration is sufficiently high (minimally a factor of 50 above the MDL in the original sample), the serial dilution (a five-fold dilution) shall then agree within 10% of the original determination after correction for dilution. If the dilution analysis for one or more analytes is not within a control limit of 10%, and the internal standards in the original sample met the contract criteria, an interference effect must be suspected, and the data for all affected analytes in the samples received and associated with that serial dilution must be flagged with an "E" on Forms IA/IB-IN and VIII-IN.

12.10.3 The percent differences for each component are calculated as follows:

EQ. 5 Serial Dilution Percent Difference

$$\%\text{Difference} = \frac{|I - S|}{I} \times 100$$

WHERE, I = Initial Sample Result (Instrument Reading)

S = Serial Dilution Result (Instrument Reading x5)

12.10.4 In the instance where there is more than one serial dilution per SDG, if one serial dilution result is not within the contract criteria, flag all samples in the SDG. Serial dilution results and "E" flags shall be reported on Form VIII-IN.

12.10.5 If the internal standard responses for the field sample chosen for serial dilution analysis are not within the limits and the appropriate corrective action (two-fold dilution and reanalysis) is taken, the following shall apply to the serial dilution analysis: if the internal standard responses of the field sample reanalysis are within the limits, the serial dilution results are to be reported

from a five-fold dilution of the reanalyzed sample. If the internal standard responses of the field sample reanalysis are not within the limits, the serial dilution results are to be reported from a five-fold dilution of the original sample.

12.11 Internal Standards

12.11.1 The analyst shall monitor the responses from the internal standards throughout the sample set being analyzed. Ratios of the internal standard responses between isotopes should also be routinely monitored. This information may be used to correct potential problems caused by mass dependent drift, errors incurred in adding the internal standards or increases in the concentrations of individual internal standards caused by background contributions from the sample. The absolute response of any one internal standard must not deviate more than 60-125% of the original response in the calibration blank. If deviations greater than these are observed in field samples, matrix spikes, or duplicate samples, the original sample shall be diluted by a factor of two, internal standards added, and the sample re-analyzed. If the internal standard responses for the diluted sample analysis are within the limits, report the results of this analysis on the appropriate Summary Form. If the internal standard responses for the diluted sample analysis are not within the limits, note this in the SDG Narrative and report the results of the undiluted original sample analysis on the appropriate Summary Form.

12.12 Method Detection Limit (MDL) Determination

12.12.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.12.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze non-prepared MDL samples on each instrument used.

12.12.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.12.4 The direct analysis MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of instrument QC.

12.12.5 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.12.6 The MDL results shall be reported on Form IX-IN.

12.13 Linear Dynamic Range (LDR)

12.13.1 Before any field samples are analyzed under this contract, the upper limit of the linear calibration range shall be established for each analyte by determining the signal responses from a minimum of three different concentration standards, one of which is close to the upper limit of the linear range, prior to the start of contract analyses

and at least quarterly thereafter. The linear calibration range used for the analysis of samples shall be determined from the resulting data. The upper LDR limit shall be an observed signal no more than 10% below the level extrapolated from lower standards. Determined sample analyte concentrations that are greater than 90% of the determined upper LDR limit must be diluted and re-analyzed. The LDRs must be verified whenever a change in instrument hardware operating conditions indicate they should be redetermined, or verified quarterly.

12.14 Example Analytical Sequence for ICP-MS

Tune
S0
S
ICV
ICB
CRI
ICSA
ICSAB
CCV
CCB
10 samples
CCV
CCB
7 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry. Method 200.8. Revision 5.4. 1994.

16.2 US Environmental Protection Agency. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (SW-846). Method 6020A. Third Edition, Update IV-A. 1986.

16.3 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

16.4 US Environmental Protection Agency. Determination of Trace Elements in Waters and Wastes by Inductively Coupled Plasma - Mass Spectrometry. Method 200.8. Revision 5.4. 1994. Modified for the Contract Laboratory Program.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Table 1. Isobaric Molecular-Ion Interferences

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{121}Sb	PdO		AgN			AgC	
^{123}Sb	AgO		AgN	SrCl	ZrS	CdC	
^{75}As	CoO	NiOH	NiN	ArCl	CaS	CuC	
^{138}Ba	SnO	SbOH					
^{137}Ba	SbO	SnOH		MoCl			
^{136}Ba	SnO	SnOH				SnC	
^{135}Ba	SnO	SnOH		MoCl			
^{134}Ba	SnO	SnOH	SnN	MoCl		SnC	
^{132}Ba	SnO, CdO	InOH	SnN	MoCl	MoS	SnC	
^{130}Ba	CdO	CdOH	SnN, CdN	MoCl	MoS	SnC	
^{9}Be							
^{114}Cd	MoO	MoOH	MoN	SeCl	SeS		
^{112}Cd	MoO, ZrO	MoOH	MoN	SeCl, AsCl	SeS	MoC	
^{111}Cd	MoO	MoOH	MoN	GeCl			
^{110}Cd	MoO, ZrO		MoN, ZrN	GeCl, AsCl	SeS	MoC	
^{113}Cd	MoO	MoOH		SeCl, AsCl			
^{116}Cd	MoO						
^{106}Cd	ZrO		MoN, ZrN		GeS	MoC, ZrC	
^{108}Cd	MoO, ZrO	ZrOH	MoN, ZrN	GeCl	SeS, GeS	MoC, ZrC	
^{52}Cr	ArO	ClOH				ArC	
^{53}Cr	ClO	ArOH	KN	NCl, OCl		KC	
^{50}Cr	SO		ArN		SO	ArC	Mo^{++}
^{54}Cr		ClOH	ArN, CaN			CaC	
^{59}Co	CaO	CaOH	ScN	MgCl	AlS	TiC	Sn^{++}
^{63}Cu	TiO, PO_2	TiOH	TiN	SiCl, MgCl	PS	VC	ArNa
^{65}Cu	TiO	TiOH	VN	SiCl	S_2, SO_2H	CrC	
^{208}Pb							
^{206}Pb							

Table 1. Isobaric Molecular-Ion Interferences (Con't)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{207}Pb							
^{204}Pb							
^{55}Mn	KO	ArOH	KN		NaS	CaC	Cd^{++}
^{202}Hg	WO						
^{200}Hg	WO	WOH	WN				
^{199}Hg	WO	WOH					
^{201}Hg		WOH					
^{198}Hg	WO	TaOH	WN			WC	
^{204}Hg							
^{196}Hg			WN			WC	
^{58}Ni	CaO	KOH	CaN	NaCl	MgS	TiC	Cd^{++}, Sn^{++}
^{60}Ni	CaO	CaOH	TiN	MgCl, NaCl	SiS	TiC	Sn^{++}
^{62}Ni	TiO	ScOH	TiN	AlCl, MgCl	SiS	TiC, CrC	Sn^{++}
^{61}Ni	ScO	CaOH	TiN	MgCl	SiS	TiC	Sn^{++}
^{64}Ni	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{80}Se	ZnO	CuOH	ZnN	ScCl, CaCl	TiS	ZnC	
^{78}Se	NiO	NiOH	ZnN	CaCl, KCl	TiS	ZnC	
^{82}Se	ZnO	CuOH	ZnN	TiCl, ScCl	TiS, CrS		
^{76}Se	NiO	CoOH	NiN	KCl	CaS	ZnC	
^{77}Se	NiO	NiOH	CuN	CaCl, ArCl	ScS	CuC	
^{74}Se	NiO	FeOH	NiN	Cl_2, KCl	CaS	NiC	
^{107}Ag	ZrO	ZrOH		GeCl	AsS	MoC	
^{109}Ag		MoOH	MoN	GeCl	SeS	MoC	
^{205}Tl							
^{203}Tl		WOH					
^{51}V	ClO	SOH	ClN	ClO, ClN	FS	KC	
^{50}V	SO		ArN			ArC	Mo^{++}
^{64}Zn	TiO	TiOH	TiN, CrN	SiCl, AlCl	S_2	CrC	
^{66}Zn	TiO	TiOH	CrN	PCl, SiCl	S_2	FeC	
^{68}Zn	CrO	VOH	FeN	PCl	ArS	FeC	Ba^{++}

Table 1. Isobaric Molecular-Ion Interferences (Con't)

Analyte	Oxygen	Hydroxyl	Nitrogen	Chlorine	Sulfur	Carbon	Other
^{67}Zn	VO	TiOH	CrN	SCl	ClS	MnC	Ba^{++}
^{70}Zn	FeO	CrOH	GeN	Cl_2	ArS	NiC	

NOTE: The information provided in this table does not indicate that all of the described interferences need to be tested. However, this table can be consulted if unusual samples are encountered.

Table 2. Mass Choices for Elements that Must Be Monitored During the Analytical Run

Mass	Element of Interest
121	Antimony
75	Arsenic
134, 135, 136, 137	Barium
9	Beryllium
111, 114	Cadmium
52, 53	Chromium
59	Cobalt
63, 65	Copper
206, 207, 208	Lead
24, 25, 26	Magnesium
55	Manganese
60, 61, 62	Nickel
77, 78, 80, 82	Selenium
107, 109	Silver
203, 205	Thallium
51	Vanadium
66, 67, 68	Zinc

NOTE: Underlined isotopes are preferred for measurements. Where possible, alternative isotopes are indicated. Those isotopes not listed shall not be used as a primary isotope for measurement, although they may be monitored for interference corrections if necessary.

Table 3. Recommended Elemental Expressions for Isobaric Interferences

Element	Isobaric Correction	Expression Proportional to Elemental Concentration
Sb	none	$(1.0000)(^{121}C)$
As	ArCl, Se	$(1.0000)(^{75}C) - (3.127)[(^{77}C) - (0.815)(^{82}C)]$
Ba	none	$(1.0000)(^{137}C)$
Be	none	$(1.0000)(^{9}C)$
Cd	MoO, Pd	$(1.000)(^{111}C) - (1.073)[(^{108}C) - (0.712)(^{106}C)]$
Cr	none	$(1.0000)(^{52}C)$
Co	none	$(1.0000)(^{59}C)$
Cu	none	$(1.0000)(^{63}C)$
Pb	none	$(1.0000)(^{206}C) + (1.0000)(^{207}C) + (1.0000)(^{208}C)$
Mn	none	$(1.0000)(^{55}C)$
Ni	none	$(1.0000)(^{60}C)$
Se	none	$(1.0000)(^{82}C)$
Ag	none	$(1.0000)(^{107}C)$
Tl	none	$(1.0000)(^{205}C)$
V	ClO, Cr	$(1.0000)(^{51}C) - (3.127)[(^{53}C) - (0.113)(^{52}C)]$
Zn	none	$(1.0000)(^{66}C)$
Sc	none	$(1.0000)(^{45}C)$
Y	none	$(1.0000)(^{89}C)$
Rh	none	$(1.0000)(^{103}C)$
In	Sn	$(1.0000)(^{115}C) - (0.0140)(^{118}C)$
Tb	none	$(1.0000)(^{159}C)$
Ho	none	$(1.0000)(^{165}C)$
Bi	none	$(1.0000)(^{209}C)$

C - Calibration blank subtracted counts at specified mass

The coefficients in correction equations were calculated using natural isotopic abundances, and assuming zero instrumental fractionation. For each particular instrument these coefficients must be determined experimentally.

The correction equations shall not be applied if appropriate interference check sample measurement demonstrates absence of interference above the CRQL.

Table 4. Internal Standards (must use at least five)

Internal Standard	Mass	CAS Number
Lithium	6	7439-93-2
Scandium	45	7440-20-2
Yttrium	89	7440-65-5
Rhodium	103	7440-16-6
Indium	115	7440-74-6
Terbium	159	7440-27-9
Holmium	165	7440-60-0
Lutetium	175	7439-94-3
Bismuth	209	7440-69-9

NOTE: Use of Li^6 requires enriched standard.

Table 5. Spiking Levels for Spike Sample Analysis

Analyte	Spike (µg/L)
Sb	100
As	40
Ba	2000
Be	50
Cd	50
Cr	200
Co	500
Cu	250
Pb	20
Mn	500
Ni	500
Se	10
Ag	50
Tl	50
V	500
Zn	500

EXHIBIT D - PART C

ANALYTICAL METHODS
FOR
COLD VAPOR MERCURY ANALYSIS

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Exhibit D - Analytical Methods for Cold Vapor Mercury Analysis

Table of Contents

Table of Contents (Con't)

1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze water, sediment, sludge, and soil samples taken from hazardous waste sites using a cold vapor technique with Atomic Absorption (AA) for total mercury.

In addition to inorganic forms of mercury, organic mercury may also be present. These organo-mercury compounds will not respond to the cold vapor AA technique unless they are first broken down and converted to mercuric ions. Potassium permanganate oxidizes many of these compounds, but studies have shown that a number of organo-mercury compounds, including phenyl mercuric acetate and methyl mercuric chloride, are only partially oxidized by this reagent. Potassium persulfate has been found to give approximately 100% recovery when used as the oxidant with these compounds. Therefore, a persulfate oxidation step following the addition of the permanganate has been included to ensure that organo-mercury compounds, if present, will be oxidized to the mercuric ion before measurement. A heat step is required for methyl mercuric chloride when present in, or spiked to, a natural system.

The range of the method may be varied through instrument and/or recorder expansion. Using a 100 milliliters (mL) sample, a detection limit of less than 0.1 micrograms per Liter (µg/L) can be achieved.

The range of the method for soil/sediments is 0.05 milligrams per kilogram (mg/kg) to 5 mg/kg. The range may be extended above or below the normal range by increasing or decreasing sample size or through instrument and recorder control.

2.0 SUMMARY OF METHOD

2.1 Water by Automated and Manual Techniques

This is a physical method based on the absorption of radiation at 253.7 nanometers (nm) by mercury vapor. Free mercury atoms can exist at room temperature; therefore, mercury can be measured by Atomic Absorption (AA) without a heated sample cell. Organic compounds are oxidized, and in the cold vapor mercury technique, mercury is chemically reduced to the free atomic state by reacting the sample with a strong reducing agent like stannous chloride or sodium borohydride in a closed reaction vessel. The volatile free mercury is then driven from the reaction flask by bubbling air through the solution. Mercury atoms are carried in the air stream through tubing connected to an absorption cell, which is placed in the light path of the AA spectrophotometer. Sometimes the cell is heated slightly to avoid water condensation; otherwise the cell is completely unheated. As the mercury atoms pass into the sampling cell, measured absorbance rises indicating the increasing concentration of mercury atoms in the light path. Some systems allow the mercury vapor to pass from the absorption tube to waste, in which case the absorption peaks and then falls as the mercury is depleted. The highest absorbance observed during the measurement will be taken as the analytical signal.

2.2 Soil/Sediment by Manual Technique

2.2.1 A weighed portion of the sample is acid digested for 2 minutes at 95°C, followed by oxidation with potassium permanganate and potassium persulfate. Mercury in the digested sample is then measured by the conventional cold vapor technique.

2.2.2 An alternate digestion involving the use of an autoclave is described in Section 10.1.4.2.1.2.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

4.1 Water

4.1.1 Some sea waters and wastewaters high in chlorides have shown a positive interference, and require additional permanganate [as much as 25 milliliters (mL)]. During the oxidation step, chlorides are converted to free chlorine which will also absorb radiation at 253 nanometers (nm). Care must be taken to assure that free chlorine is absent before the mercury is reduced and swept into the cell. This may be accomplished by using an excess of hydroxylamine sulfate reagent (25 mL). Both inorganic and organic mercury spikes have been quantitatively recovered from the sea water using this technique.

4.1.2 Formation of a heavy precipitate, in some wastewaters and effluents, has been reported upon addition of concentrated sulfuric acid. If this is encountered, the problem sample cannot be analyzed by this method.

4.1.3 Possible interference from sulfide is eliminated by the addition of potassium permanganate. Concentrations as high as 20 milligram per Liter (mg/L) of sulfide as sodium sulfide do not interfere with the recovery of added inorganic mercury from reagent water.

4.1.4 Copper has also been reported to interfere; however, copper concentrations as high as 10 mg/L have no effect on recovery of mercury from spiked samples.

4.1.5 Samples containing solids must be blended and then mixed while being sampled if total mercury values are to be reported.

4.2 Soil/Sediment

4.2.1 The same types of interferences that may occur in water samples are also possible with sediments (i.e., sulfides, high copper, high chlorides, etc.).

4.2.2 Samples containing high concentrations of oxidizable organic materials, as evidenced by high chemical oxygen demand values, may not be completely oxidized by this procedure. When this occurs, the recovery of organic mercury will be low. The problem can be eliminated by reducing the weight of the original sample or by increasing the amount of potassium persulfate (and consequently stannous chloride) used in the digestion.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 General Information for Water and Soils (Automated and Manual Techniques)

6.1.1 Atomic Absorption (AA) Spectrophotometer - Any AA unit having an open sample presentation area in which to mount the absorption cell is suitable. Instrument settings recommended by the particular manufacturer should be followed.

NOTE: Instruments designed specifically for the measurement of mercury using the cold vapor technique are commercially available and may be substituted for the AA spectrophotometer.

NOTE: All cold vapor mercury analyzers shall be equipped with all manufactured required equipment (i.e., dryers) to ensure that the specified CRQLs are met.

6.1.2 Mercury Hollow Cathode Lamp

6.1.3 Recorder - Any multi-range variable speed recorder that is compatible with the UV detection system is suitable.

6.2 Water by Automated Technique

6.2.1 Automated Analyzer instrumentation consisting of:

6.2.1.1 Sampler with provision for sample mixing

6.2.1.2 Manifold

6.2.1.3 Proportioning Pump(s)

6.2.1.4 High temperature heating bath with distillation coil(s)

6.2.1.5 Vapor-liquid separator

6.2.1.6 Absorption cell with quartz windows

6.3 Water and Soil/Sediment by Manual Technique

6.3.1 Absorption Cell - Standard spectrophotometer cells

6.3.2 Air Pump - Any device capable of delivering 1 Liter (L) of air per minute may be used.

6.3.3 Flowmeter - Capable of measuring an air flow of 1 L per minute.

6.3.4 Aeration Tubing - Tygon tubing is used for transporting the mercury vapor from the sample bottle to the absorption cell and for its return.

6.3.4.1 Straight glass tubing terminating in a coarse porous frit is used for sparging air into the sample.

6.3.5 Drying Tube - 6" X 3/4" diameter tube containing 20 grams (g) of magnesium perchlorate.

NOTE: In place of the magnesium perchlorate drying tube, a small reading lamp with a 60-watt bulb may be used to prevent condensation of moisture inside the cell. The lamp is positioned to shine on the absorption cell maintaining the air temperature in the cell about 10°C above ambient temperature.

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Water by Automated Technique

7.1.1.1 Reagent Water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.1.2 Sulfuric acid, concentrated - Reagent grade.

7.1.1.2.1 Sulfuric acid, 2N - Dilute 56 milliliters (mL) of concentrated sulfuric acid to 1 Liter (L) with reagent water.

7.1.1.2.2 Sulfuric acid, 10% - Dilute 100 mL concentrated sulfuric acid to 1 L with reagent water.

7.1.1.3 Nitric acid, concentrated - Reagent grade of low mercury content.

Nitric acid, 0.5% wash solution - Dilute 5 mL of concentrated nitric acid to 1 L with reagent water.

7.1.1.4 Stannous sulfate - Add 50 grams (g) stannous sulfate to 500 mL of 2N sulfuric acid (see Section 7.1.1.2.1). This mixture is a suspension and should be stirred continuously during use.

NOTE: Stannous chloride may be used in place of stannous sulfate.

7.1.1.5 Sodium chloride-hydroxylamine sulfate solution - Dissolve 30 g of sodium chloride and 30 g of hydroxylamine sulfate in reagent water to 1 L.

NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.1.1.6 Potassium permanganate ($KMnO_4$) - 0.5% solution, w/v. Dissolve 5 g of potassium permanganate in 1 L of reagent water.

7.1.1.7 Potassium permanganate, 0.1N - Dissolve 3.16 g of potassium permanganate in reagent water and dilute to 1 L.

7.1.1.8 Potassium persulfate - 0.5% solution, w/v. Dissolve 5 g of potassium persulfate in 1 L of reagent water.

7.1.1.9 Air scrubber solution - Mix equal volumes of 0.1N potassium permanganate (see Section 7.1.1.6) and 10% sulfuric acid (see Section 7.1.1.2.2).

7.1.2 Water and Soil/Sediment by Manual Technique

7.1.2.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2.2 Sulfuric acid, concentrated - Reagent grade.

7.1.2.2.1 Sulfuric acid, 0.5N - Dilute 14.0 mL of concentrated sulfuric acid to 1 L. (Water technique only.)

7.1.2.3 Nitric acid, concentrated - Reagent grade of low mercury content. If a high Preparation Blank (PB) is obtained, it may be necessary to distill the nitric acid.

7.1.2.4 Stannous sulfate - Add 25 g stannous sulfate to 250 mL of 0.5N sulfuric acid. This mixture is a suspension and should be stirred continuously during use.

NOTE: Stannous chloride may be used in place of stannous sulfate.

7.1.2.5 Sodium chloride-hydroxylamine sulfate solution - Dissolve 12 g of sodium chloride and 12 g of hydroxylamine sulfate in reagent water and dilute to 100 mL.

NOTE: Hydroxylamine hydrochloride may be used in place of hydroxylamine sulfate.

7.1.2.6 Potassium permanganate ($KMnO_4$) - 5% solution, w/v. Dissolve 5 g of potassium permanganate in 100 mL of reagent water.

7.1.2.7 Potassium persulfate - 5% solution, w/v. Dissolve 5 g of potassium persulfate in 100 mL of reagent water.

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.1.1 Stock standard solutions may be purchased or prepared from reagent grade chemicals or metals.

7.2.1.2 Stock mercury solution - Dissolve 0.1354 g of mercuric chloride in 75 mL of reagent water. Add 10 mL of concentrated nitric acid and adjust the volume to 100.0 mL [1.0 mL = 1.0 milligram (mg) Hg].

7.2.1.3 Working mercury solution - Make successive dilutions of the stock mercury solution (see Section 7.2.1.2) to obtain a working standard containing 0.1 micrograms (µg) per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards.

7.2.2 Working Standards

7.2.2.1 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

The concentration of the CRI for mercury shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

7.2.2.2 Method Detection Limit (MDL) Solution

The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

All samples must be collected in glass or polyethylene containers. Water/aqueous samples must be preserved with nitric acid to pH less than 2 immediately after collection. All samples must be iced or refrigerated at 4°C (±2°C) from the time of collection until digestion.

8.1.1 Dissolved Metals

For the determination of dissolved metals, the sample must be filtered through a 0.45 micrometer (µm) pore diameter membrane filter at the time of collection or as soon as possible. Use a portion of the sample to rinse the filter flask, discard this portion, and collect the required volume of filtrate. Preserve the filtrate with nitric acid to pH less than 2 immediately after filtration.

8.2 Procedure for Sample Storage

The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.3 Contract Required Holding Time

The maximum holding time for mercury is 26 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Cold Vapor Atomic Absorption (AA) Instrument Calibration Procedure

9.1.1 Instruments shall be calibrated daily or once every 24 hours and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.1.2 The date and time of preparation and analysis shall be given in the raw data.

9.1.3 Calibration standards shall be prepared fresh with each preparation batch. Prepare a minimum of five calibration standards (which includes a blank) in graduated amounts in the appropriate range. One of the standards must be at the Contract Required Quantitation Limit (CRQL).

9.1.4 Aspirate the standards and record the readings. Results for these standards shall be within 5% of the true value. Each standard concentration and the calculations to show that the 5% criteria has been met shall be given in the raw data. If the values do not fall within this range, recalibration is necessary. The 5% criteria does not apply to the calibration standard at the CRQL. The acceptance criteria for the initial calibration curve is a correlation coefficient more than or equal to 0.995.

9.1.5 Baseline correction is acceptable as long as it is performed after every sample or after the Continuing Calibration Verification (CCV) and Blank (CCB) check. Resloping is acceptable as long as it is immediately preceded and immediately followed by a compliant CCV and CCB.

9.2 Initial Calibration Verification (ICV)

9.2.1 Immediately after the AA system has been calibrated, the accuracy of the initial calibration shall be verified and documented for mercury by the analysis of the ICV solution at the wavelength used for analysis.

9.2.2 Only if the ICV solution is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but within the calibration range. An independent standard is defined as a standard composed of the analyte from a different source than that used in the standards for the instrument calibration. The value for the ICV shall be reported on Form IIA-IN.

9.3 Continuing Calibration Verification (CCV)

9.3.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported at the beginning of the run and after the last analytical sample. The analyte concentration in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near the mid-range level of the calibration curve:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.3.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.3.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.4 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at each wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90% of the required amount) is received to perform the analyses, the Contractor shall contact the Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multiphase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprise them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample, and analyze one or more of the phases separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside the scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Water Preparation of Standards and Samples (Manual Technique)

10.1.3.1 Standards Preparation

10.1.3.1.1 Transfer aliquots of the working mercury solution to a series of 300 milliliters (mL) BOD bottles or other suitable digestion vessels. Add enough reagent water to each bottle to make a total volume of 50-100 mL.

10.1.3.1.2 Mix thoroughly and add 5 mL of concentrated sulfuric acid (see Section 7.1.2.2) and 2.5 mL of concentrated nitric acid (see Section 7.1.2.3) to each bottle. Add 15 mL of $KMnO_4$ (see Section 7.1.2.6) solution to each bottle and allow to stand at least 15 minutes. Add 8 mL of potassium persulfate (see Section 7.1.2.7) to each bottle and heat for 2 hours in a water bath or block digester maintained at 95°C. (If an autoclave is employed, cover the BOD bottles with foil and heat in the autoclave for 15 minutes at 120°C and 15 PSI instead of heating for 2 hours in a waterbath at 95°C). Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section

7.1.2.5) to reduce the excess permanganate. When the solution has been decolorized, wait 30 seconds, add 5 mL of the stannous sulfate solution (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus to form a closed system. At this point the sample is allowed to stand quietly without manual agitation. If volumes less than 100 mL are used, all other reagents shall be reduced accordingly (e.g., if 50 mL is used, reduce reagent volumes by one-half).

10.1.3.1.3 The circulating pump, which has previously been adjusted to a rate of 1 Liter (L) per minute, is allowed to run continuously (see Note 1). The absorbance will increase and reach maximum within 30 seconds. As soon as the response levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value (see Note 2). Close the bypass valve, remove the stopper and frit from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting instrument response at 253 nanometers (nm) versus micrograms (µg) of mercury.

NOTE 1: An open system where the mercury vapor is passed through the absorption cell only once may be used instead of the closed system.

NOTE 2: Because of the toxic nature of mercury vapor, precaution must be taken to avoid its inhalation. Therefore, a bypass has been included in the system to either vent the mercury vapor into an exhaust hood or pass the vapor through some absorbing media, such as equal volumes of 0.1 M $KMnO_4$, and 10% H_2SO_4 or 0.25% iodine in a 3% KI solution. A specially treated charcoal that will adsorb mercury vapor is commercially available.

10.1.3.2 Sample Preparation

10.1.3.2.1 Preparation Method/Code (CW1)

10.1.3.2.1.1 Transfer 50-100 mL, or an aliquot diluted to 50-100 mL, containing not more than 1.0 µg of mercury, to a 300 mL BOD bottle or other suitable digestion vessel, and continue as described in Section 10.1.3.1.2.

NOTE: The same amount of $KMnO_4$ added to the samples should be present in standards and blanks.

10.1.3.2.1.2 Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (see Section 7.1.2.5) to reduce the excess permanganate. Purge the headspace in the BOD bottle for at least 1 minute and add 5 mL of stannous sulfate (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus.

NOTE: Add reductant in 6 mL increments until $KMnO_4$ is completely reduced (until the color is no longer purple).

10.1.4 Soil/Sediment Preparation of Standards and Samples (Manual)

10.1.4.1 Standards Preparation

10.1.4.1.1 Transfer aliquots of the working mercury solutions (see Section 7.2.1.3) to a series of 300 mL BOD bottles or other suitable digestion vessels. Add enough reagent water to each bottle to make a total volume of 10 mL.

10.1.4.1.2 Add 5 mL of concentrated H_2SO_4 (see Section 7.1.2.2) and 2.5 mL of concentrated HNO_3 (see Section 7.1.2.3) and heat 2 minutes in a water bath or block digester at 95°C. Allow the sample to cool and add 50 mL reagent water, 15 mL of $KMnO_4$ solution (see Section 7.1.2.6) and 8 mL of potassium persulfate solution (see Section 7.1.2.7) to each bottle and return to the water bath or block digester for 30 minutes. Cool and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section 7.1.2.5) to reduce the excess permanganate. Add 50 mL of reagent water (final volume of reagent water = 100 mL). Treating each bottle individually, add 5 mL of stannous sulfate solution (see Section 7.1.2.4) and immediately attach the bottle to the aeration apparatus. At this point the sample is allowed to stand quietly without manual agitation. If an autoclave is used, the standards shall be prepared in the same way as the samples (see Section 10.1.4.2.1.2).

10.1.4.1.3 The circulating pump, which has previously been adjusted to a rate of 1 L per minute, is allowed to run continuously. The absorbance, as exhibited either on the spectrophotometer or the recorder, will increase and reach maximum within 30 seconds. As soon as the response levels off, open the bypass valve and continue the aeration until the absorbance returns to its minimum value. Close the bypass valve, remove the fritted tubing from the BOD bottle and continue the aeration. Proceed with the standards and construct a standard curve by plotting peak height versus µg of mercury.

10.1.4.2 Sample Preparation

10.1.4.2.1 Preparation Method/Code (CS1)

10.1.4.2.1.1 Weigh a representative 0.20 g (±0.01 g) portion of wet sample and place in the bottom of a BOD bottle. Add enough reagent water to each sample to make a total volume of 10 mL. Continue as described in Section 10.1.4.1.2.

10.1.4.2.1.2 If an autoclave is used, add 5 mL of concentrated H_2SO_4 and 2 mL of concentrated HNO_3 to the 0.20 g (±0.01 g) of sample. Add 5 mL of saturated $KMnO_4$ solution and 8 mL of potassium persulfate solution and cover with a piece of aluminum foil. The sample is autoclaved at 120°C and 15 PSI for 15 minutes. Cool, make up to a volume of 100 mL with reagent water, and add 6 mL of sodium chloride-hydroxylamine sulfate solution (see Section 7.1.2.5) to reduce the excess permanganate. Purge the headspace of the sample bottle for at least one minute and continue as described under Section 10.1.4.1.2.

10.1.5 Preparation of Standards for Automated Cold Vapor Analysis Technique (Analysis Method - AV)

10.1.5.1 Standards Preparation

Make successive dilutions of the stock mercury solution to obtain a working standard containing 0.1 µg per mL. This working standard and the dilutions of the stock mercury solution should be prepared fresh daily. Acidity of the working standard should be maintained at 0.15% nitric acid. This acid should be added to the flask as needed before the addition of the aliquot. From this solution, prepare standards.

10.2 Sample Analysis

10.2.1 Set up instrument with proper operating parameters.

10.2.2 Profile and calibrate instrument according to instrument manufacturer's recommended procedures, using calibration standard solutions mentioned in Section 9.1. Samples prepared by a certain method must be analyzed with calibration and QC standards prepared by the same method. Therefore, only one Preparation Method/Code can be associated with each run.

10.2.3 Analyze the Continuing Calibration Verification (CCV) instrument check standard and the Continuing Calibration Blank (CCB) after every 10 analytical samples.

10.2.4 Analysis of Water/Aqueous Samples by the Automated Cold Vapor Technique (AV) Preparation Method/Code (CW2)

10.2.4.1 Set up manifold.

10.2.4.2 Feed all the reagents through the system with acid wash solution (see Section 7.1.1.3) through the sample line, adjusting the heating bath to 105°C.

10.2.4.3 Turn on the Atomic Absorption (AA) Spectrophotometer, adjust instrument settings as recommended by the manufacturer, align absorption cell in light path for maximum transmittance and place heat lamp directly over absorption cell.

10.2.4.4 Arrange working mercury standards in sampler and start sampling. Complete loading of sample tray with unknown samples.

10.2.4.5 After the analysis is complete, put all lines except the H_2SO_4 line in reagent water to wash out system. After flushing, wash out the H_2SO_4 line. Also flush the coils in the high temperature heating bath by pumping stannous sulfate (see Section 7.1.1.4) through the sample lines followed by reagent water. This will prevent build-up of oxides of manganese.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous by Automated Technique

11.1.1 Prepare a standard curve by plotting the instrumental response of processed standards against true concentration values. Use a linear regression equation to determine the concentration of field and Quality Control (QC) samples.

11.1.2 If samples were diluted for analysis, multiply the results from the linear regression by the dilution factor.

11.2 Water/Aqueous by Manual Technique

11.2.1 Determine the instrumental response of the unknown and determine the mercury value from the standard curve.

11.2.2 Calculate the mercury concentration in the sample by the formula:

EQ. 1 Aqueous Sample Concentration (Manual)

$$\text{Hg Concentration } (\mu g/L) = \frac{\mu g \text{ Hg, curve}}{\text{aliquot volume, mL}} \times \frac{1000 \text{ mL}}{1 \text{ L}}$$

11.3 Soil by Manual Technique

11.3.1 Measure the instrumental response of the unknown and determine the mercury value from the standard curve.

11.3.2 Calculate the mercury concentration in the sample by the formula:

EQ. 2 Soil Sample Concentration (Manual)

$$\text{Hg Concentration (mg/kg)} = \text{Hg } \mu g/g = \frac{C}{W \times S} \times (0.1L)$$

WHERE, C = Concentration from curve (µg/L)

W = Wet sample weight (g)

S = % Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.4 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted MDL or adjusted CRQL for water/aqueous samples, multiply the value of the MDL (µg/L) or CRQL (µg/L) by the Dilution Factor. Calculate the adjusted MDL or adjusted CRQL for soil samples as follows:

EQ. 3 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (dry wt.)(mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S} \times DF$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	Method required wet sample weight (g)
W_R	=	Reported wet sample weight (g)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).
DF	=	Dilution Factor

12.0 QUALITY CONTROL

12.1 Initial Calibration Verification (ICV)

The ICV Standard shall be prepared in the same acid matrix as the samples and carried through the entire preparation and analysis procedure. If measurements exceed the control limits of 80% (low) and 120% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV Standard shall be prepared by the analyst at a concentration equivalent to the mid-point of the calibration curve and carried through the entire preparation and analysis procedure. If the deviation of the CCV is greater than the control limits of 80% (low) and 120% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, the Contractor shall analyze a CRI at the beginning and end of each sample analysis run, immediately following the ICV/ICB. In addition, the Contractor shall analyze and report the results for the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. The CRI analysis shall be run immediately followed by the CCV and Continuing Calibration Blank (CCB) analyses. The CRI shall be prepared by spiking an aliquot of reagent water with mercury at the CRQL. The CRI shall be taken through the same process used to digest and analyze the associated samples.

12.3.2 CRI and percent recovery results shall be reported on Form IIB-IN. If the percent recovery falls outside the control limits of 70-130%, the CRI shall be re-analyzed immediately. If the result of the re-analysis falls within the control limits, no further corrective action is required. If the result of the re-analysis does not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, or the CRI and associated samples redigested and analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with acids and reagent water and carried through the entire preparation and analysis procedure. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical

[1]As defined in Exhibit G, CRI is an analytical sample.

samples analyzed since the last compliant calibration blank shall be performed.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same acid concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples digested, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with that blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redigested and re-analyzed with appropriate new Quality Control (QC). The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples reported below 10 times the CRQL and associated with the blank shall be redigested and re-analyzed with appropriate new QC.

12.4.2.4.4 The values for the PB shall be reported on Form III-IN.

12.5 Spike Sample Analysis

12.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the digestion and/or measurement methodology. The spike is added before the digestion (i.e., prior to the addition of other reagents). At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[3] The sample

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[2]A group of samples prepared at the same time.

[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

and its associated spike sample shall initially be run at the same dilution.

12.5.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.6). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.5.3 The analyte spike shall be added at 1 µg/L (water) or 0.5 mg/kg (soil). Adjustment shall be made to maintain these spiking levels when the weight of sample taken deviates by more than 10% of these values.

12.5.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample and determined by the same analytical method shall be flagged with the letter "N" on Forms IA-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.5.5 In the instance where there is more than one spike sample per matrix, per method, per SDG, and one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries (%R) are calculated as follows:

EQ. 4 Spike Percent Recovery

$$\%\ \text{Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE, SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.5.6 When sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.5.7 The units used for reporting SSRs will be identical to those used for reporting sample results on Form IA-IN.

12.6 Duplicate Sample Analysis

12.6.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4] Duplicates cannot be averaged for reporting on Form IA-IN. The

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

sample and its associated duplicate sample shall initially be run at the same dilution.

12.6.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 5 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE, RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.6.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.6.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received associated with that duplicate sample with an "*" on Forms IA-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix and method in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for each element will be added to Form VI-IN at a later date based on these precision results.

12.7 Laboratory Control Sample (LCS) Analysis

12.7.1 A solid LCS (LCSS) shall be analyzed using the same sample preparations, analytical methods, and Quality Assurance (QA)/QC procedures employed for the EPA samples received.

12.7.2 The USEPA provided LCSS shall be prepared and analyzed using the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check samples or other certified materials may be used. In such a case, control limits for the LCSS must be documented and provided. One LCSS shall be prepared and

analyzed for every group of solid samples in a SDG, or for each batch of samples digested, whichever is more frequent.

12.7.3 All LCSS and percent recovery results will be reported on Form VII-IN. If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS redigested and re-analyzed with appropriate new QC.

12.8 Method Detection Limit (MDL) Determination

12.8.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for each digestion procedure and instrument used, prior to the start of contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions, to verify the current sensitivity of the analysis.

12.8.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall prepare the MDL samples by each digestion procedure used and shall analyze these samples on each instrument used.

12.8.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.8.4 The results of the MDL determination studies shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.8.5 The MDL results shall be reported on Form IX-IN.

12.9 Example Analytical Sequence for Mercury

S0
S0.2
S0.5
S1.0
S2.0
S5.0
S10.0
ICV
ICB
CRI
CCV
CCB
10 samples
CCV
CCB
9 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.1. 1974.

16.2 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.2. 1974.

16.3 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 245.5. 1974.

16.4 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.

EXHIBIT D - PART D

ANALYTICAL METHODS
FOR
TOTAL CYANIDE ANALYSIS

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Exhibit D - Analytical Methods for Total Cyanide Analysis

Table of Contents

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1.0 SCOPE AND APPLICATION

The analytical method that follows is designed to analyze various water types, sediment, sludge, and soil samples taken from hazardous waste sites, for total cyanide.

This analytical method includes the use of acid and heat to remove cyanide from the sample.

2.0 SUMMARY OF METHOD

2.1 Waters and Soils

2.1.1 The cyanide as hydrocyanic acid (HCN) is released from cyanide complexes by means of a reflux-distillation and absorbed in a scrubber containing sodium hydroxide solution. The cyanide ion in the absorbing solution is then determined colorimetrically.

2.1.2 In the colorimetric measurement, the cyanide is converted to cyanogen chloride (CNCl), by reaction with chloramine-T at a pH less than 8 without hydrolyzing to the cyanate. After the reaction is complete, color is formed on the addition of pyridine-barbituric acid reagent. The absorbance is read between 570 and 580 nanometers (nm). To obtain colors of comparable intensity, it is essential to have the same salt content in both the sample and the standards.

3.0 DEFINITIONS

See Exhibit G for a complete list of definitions.

4.0 INTERFERENCES

Interferences are eliminated or reduced by using the distillation procedure.

4.1 Sulfides

Sulfides adversely affect the colorimetric procedure. The sample should be tested in the field for the presence of sulfides as described in Section 8.1.1.

4.2 Surfactants

The presence of surfactants may cause the sample to foam during refluxing. If this occurs, the addition of an agent such as Dow Corning 544 antifoam agent will prevent the foam from collecting in the condenser.

4.3 Oxidizing Agents

Oxidizing agents such as chlorine decompose most of the cyanides. The sample should be tested in the field for the presence of oxidizing agents as described in Section 8.1.1.

5.0 SAFETY

See Section 1.14 in Exhibit D - Introduction to Analytical Methods.

6.0 EQUIPMENT AND SUPPLIES

Brand names, suppliers, and part numbers are for illustrative purposes only. No endorsement is implied. Equivalent performance may be achieved using equipment and supplies other than those specified here, however, a demonstration of equivalent performance meeting the requirements of this Statement of Work (SOW) is the responsibility of the Contractor. The Contractor shall document any use of alternate equipment or supplies in the Sample Delivery Group (SDG) Narrative.

6.1 Conventional Distillation of Water and Soils

6.1.1 Reflux distillation apparatus. The boiling flask should be of 1 Liter (L) size with an inlet tube and provision for condenser. The gas absorber may be a Fisher-Milligan scrubber.

6.1.2 Spectrophotometer suitable for measurements between 570 and 580 nanometers (nm) with a 1.0 centimeter (cm) cell or larger (for manual spectrophotometric method).

6.1.3 Automated analyzer instrumentation (for automated spectrophotometric method) including:

6.1.3.1 Sampler

6.1.3.2 Pump

6.1.3.3 Cyanide manifold

6.1.3.4 Colorimeter with 15 millimeters (mm) flow cells and 580 nm filters

6.1.3.5 Recorder

6.1.3.6 Data system (optional)

6.1.3.7 Glass or plastic tubes for the sampler

6.2 Midi Distillation of Water and Soils

6.2.1 Midi reflux distillation apparatus

6.2.2 Heating block - Capable of maintaining 125°C (±5°C).

6.2.3 Auto analyzer system with accessories:

6.2.3.1 Sampler

6.2.3.2 Pump

6.2.3.3 Cyanide cartridge

6.2.3.4 Colorimeter with 50 mm flow cells and 580 nm filter

6.2.3.5 Chart recorder or data system

6.2.4 Assorted volumetric glassware, pipets, and micropipets

7.0 REAGENTS AND STANDARDS

7.1 Reagents

7.1.1 Reagent water - The purity of this water must be equivalent to ASTM Type II water (ASTM D1193-77). Use this preparation for all reagents, standards, and dilutions of solutions.

7.1.2 Conventional Distillation and Preparation Reagents of Water and Soils

7.1.2.1 Sodium hydroxide solution, 1.25N - Dissolve 50 grams (g) of NaOH in reagent water, and dilute to 1 Liter (L) with reagent water. (Same Distillation and Preparation Reagent for Midi Distillation of Water and Soils.)

7.1.2.2 Cadmium carbonate - Powdered

7.1.2.3 Ascorbic acid - Crystals

7.1.2.4 Sulfuric acid - Concentrated

7.1.2.5 Hydrochloric acid (HCl) - Concentrated (specific gravity 1.19).

7.1.2.6 Magnesium chloride solution - Weigh 510 g of $MgCl_2 \cdot 6H_2O$ into a 1000 milliliter (mL) flask, dissolve, and dilute to 1 L with reagent water. (Same Distillation and Preparation Reagent for Midi Distillation of Water and Soils.)

7.1.3 Midi Distillation and Preparation Reagents of Water and Soils

7.1.3.1 Sodium hydroxide absorbing solution and sample wash solution, 0.25N - Dissolve 10.0 g NaOH in reagent water and dilute to 1 L.

7.1.3.2 Sulfuric acid, 50% (v/v) - Carefully add a portion of concentrated H_2SO_4 to an equal portion of reagent water.

7.1.4 Manual Spectrophotometric Reagents for Water and Soils

7.1.4.1 Acetate Buffer - Dissolve 410 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 500 mL of reagent water. Add sufficient glacial acetic acid to adjust pH to 4.5 (approximately 500 mL).

7.1.4.2 Chloramine-T solution - Dissolve 1.0 g of white, water soluble chloramine-T in 100 mL of reagent water and refrigerate until ready to use. Prepare fresh weekly.

7.1.4.3 Color Reagent

7.1.4.3.1 Pyridine-barbituric acid reagent - Place 15 g of barbituric acid in a 250 mL volumetric flask and add just enough reagent water to wash the sides of the flask and wet the barbituric acid. Add 75 mL of pyridine and mix. Add 15 mL of HCl (specific gravity 1.19), mix, and cool to room temperature. Dilute to 250 mL with reagent water and mix. This reagent is stable for approximately six months if stored in a cool, dark place.

7.1.5 Semi-Automated Spectrophotometric Reagents for Conventional and Midi Distillation of Water and Soils

7.1.5.1 Chloramine-T solution - Dissolve 0.40 g of chloramine-T in reagent water and dilute to 100 mL. Prepare fresh daily.

7.1.5.2 Acetate Buffer - Dissolve 410 g of $NaC_2H_3O_2 \cdot 3H_2O$ in 500 mL of reagent water. Add sufficient glacial acetic acid to adjust pH to 4.5 (approximately 500 mL).

7.1.5.3 Pyridine-barbituric acid solution - Transfer 15 g of barbituric acid into a 1 liter volumetric flask. Add about 100 mL of reagent water and swirl the flask. Add 75 mL of pyridine and mix. Add 15 mL of concentrated HCl and mix. Dilute to about 900 mL with reagent water and mix until the barbituric acid is dissolved. Dilute to 1 L with reagent water. Store at 4°C (±2°C).

7.1.5.4 Sampler wash - Dissolve 10 g of NaOH in reagent water and dilute to 1 L. (For conventional distillation of water and soils only.)

7.2 Standards

7.2.1 Introduction

The Contractor must provide all standards to be used with this contract. These standards may be used only after they have been certified according to the procedure in Exhibit E, Section 8.0. The Contractor must be able to verify that the standards are certified. Manufacturer's certificates of analysis must be retained by the Contractor and presented upon request.

7.2.2 Stock Standard Solutions

7.2.2.1 Stock Standard Reagents for Water and Soils

7.2.2.1.1 Stock cyanide solution - Dissolve 2.51 g of KCN and 2 g KOH in 1 L of reagent water. Standardize with 0.0192N $AgNO_3$.

7.2.2.1.2 Standard cyanide solution, intermediate - Dilute 50.0 mL of stock (1 mL = 1 milligram (mg) CN) to 1000 mL with reagent water.

7.2.2.1.3 Standard cyanide solution - Prepare fresh daily by diluting 100 mL of intermediate cyanide solution to 1000 mL with reagent water and store in a glass stoppered bottle. 1 mL = 5.0 micrograms (µg) CN [5.0 milligrams per Liter (mg/L)].

7.2.2.1.4 Sodium hydroxide solution, 0.25N - Dissolve 10 g of NaOH in reagent water and dilute to 1 L.

7.2.2.2 Stock Standard Reagents for Midi Distillation of Water and Soils

7.2.2.2.1 Stock cyanide solution, 1000 mg/L CN - Dissolve 2.51 g of KCN and 2.0 g KOH in reagent water and dilute 1 L. Standardize with 0.0192N $AgNO_3$.

7.2.2.2.2 Intermediate cyanide standard solution, 10 mg/L CN - Dilute 1.0 mL of stock cyanide solution (see Section 7.2.2.2.1) plus 20 mL of 1.25N NaOH solution (see Section 7.1.2.1) to 100 mL with reagent water. Prepare this solution at time of analysis.

7.2.2.2.3 Sodium hydroxide solution, 0.1N - Dissolve 4 g of NaOH in reagent water and dilute to 1 L.

7.2.3 Secondary Dilution Standards

7.2.3.1 Secondary Dilution Standards

Prepare secondary dilution standard solutions by diluting the appropriate volumes of stock standards with 0.25N NaOH. The final concentration of NaOH in all standards should be 0.25N.

7.2.4 Working Standards

7.2.4.1 Method Detection Limit (MDL) Solution

7.2.4.1.1 The MDL solution shall be at a concentration of 3 to 5 times the expected MDL.

7.2.4.2 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

7.2.4.2.1 The concentration of the CRI for cyanide shall be at the CRQL. Information regarding the CRI shall be reported on Form IIB-IN.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection and Preservation

8.1.1 Water Sample Preservation

Collection of total cyanide must be in polyethylene or glass containers. The sample must be tested for sulfides and oxidizing agents, and preserved by the sampler immediately upon sample collection. Place a drop of the sample on lead acetate test paper (which has been pre-moistened with pH 4 acetate buffer solution) to detect the presence of sulfides. If sulfides are present (test strip turns black), the sample volume required for the cyanide determination should be increased by 25 milliliters (mL). The total volume of sample should then be treated with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates if the sample contains sulfide. Repeat this operation until a drop of the treated sample solution does not darken the lead acetate test paper. Filter the solution through a dry filter paper into a dry beaker, and from the filtrate measure the sample to be used for analysis. Avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the precipitated material. If no sulfides are present, test for the presence of oxidizing agents by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper); a blue color indicates the need for treatment. Add ascorbic acid, a few crystals at a time, until a drop of sample produces no color on the indicator paper. Then add an additional 0.6 gram (g) of ascorbic acid for each liter of sample volume. Preserve the sample with NaOH to pH greater than 12 and maintain at 4°C (±2°C) until distillation.

8.1.2 Soil/Sediment Sample Preservation

Samples shall be kept at 4°C (±2°C) from the time of collection until distillation.

8.2 Procedure for Sample Storage

8.2.1 The samples must be protected from light and refrigerated at 4°C (±2°C) from the time of receipt until 60 days after delivery of a complete, reconciled data package to the USEPA. After 60 days the samples may be disposed of in a manner that complies with all applicable regulations.

8.2.2 The samples must be stored in an atmosphere demonstrated to be free of all potential contaminants.

8.2.3 Samples, sample distillates, and standards must be stored separately.

8.3 Contract Required Holding Time

The maximum sample holding time for cyanide is 12 days from Validated Time of Sample Receipt (VTSR).

9.0 CALIBRATION AND STANDARDIZATION

9.1 Instrument Operating Parameters

Because of the difference between various makes and models of satisfactory instruments, no detailed operating instructions can be provided. The analyst should follow the instructions provided by the manufacturer of the particular instrument. It is the responsibility of the analyst to verify that the instrument configuration and operating conditions used satisfy the analytical requirements and to maintain Quality Control (QC) data confirming instrument performance and analytical results.

9.2 General Procedure

The following general procedure applies to most semi-automated colorimeters. Set up the manifold and complete system per manufacturer's instructions. Allow the colorimeter and recorder to warm up for at least 30 minutes prior to use. Establish a steady reagent baseline, feeding reagent water through the sample line and appropriate reagents (see Section 7.1.5) through reagent lines. Adjust the baseline using the appropriate control on the colorimeter. Prepare a standard curve by plotting absorbance of standard vs. cyanide concentrations [per 250 milliliter (mL)].

9.3 Spectrophotometric Instrument Calibration Procedure

9.3.1 Instruments shall be calibrated daily or once every 24 hours, and each time the instrument is set up. The instrument standardization date and time shall be included in the raw data.

9.3.2 The date and time of preparation and analysis shall be given in the raw data.

9.3.3 Calibration standards shall be prepared fresh daily or each time an analysis is to be made and discarded after use. Prepare a blank and at least three calibration standards in graduated amounts in the appropriate range. One of the calibration standards shall be at the Contract Required Quantitation Limit (CRQL). The acceptance criteria for the initial calibration curve is a correlation coefficient greater than or equal to 0.995.

9.3.4 Any changes or corrections to the analytical system shall be followed by recalibration.

9.3.5 Baseline correction is acceptable as long as it is performed after every sample or after the Continuing Calibration Verification (CCV) and Blank (CCB) check. Resloping is acceptable as long as it is immediately preceded and immediately followed by a compliant CCV and CCB.

9.4 Initial Calibration Verification (ICV)

9.4.1 Immediately after each cyanide system has been calibrated, the accuracy of the initial calibration shall be verified and documented for cyanide by the analysis of the ICV Solution at the wavelength used for analysis.

9.4.2 Only if the ICV Solution is not available from USEPA, or where a certified solution of the analyte is not available from any source, analyses shall be conducted on an independent standard at a concentration other than that used for instrument calibration, but

within the calibration range. An independent standard is defined as a standard composed of the analytes from a different source than those used in the standards for the instrument calibration.

9.4.3 The ICV shall be distilled. This means that an ICV must be distilled with each batch of samples analyzed and that the samples distilled with an ICV must be analyzed with that particular ICV.

9.4.4 The value for the ICV shall be reported on Form IIA-IN.

9.5 Continuing Calibration Verification (CCV)

9.5.1 To ensure calibration accuracy during each analysis run, one of the following standards is to be used for the CCV and shall be analyzed and reported at a frequency of 10% or every 2 hours during an analysis run, whichever is more frequent. The standard shall also be analyzed and reported at the beginning of the run and after the last analytical sample. The analyte concentration in the CCV standard shall be different than the concentration used for the ICV and shall be one of the following solutions at or near the mid-range level of the calibration curve:

- USEPA Solutions
- NIST Standards
- A Contractor-prepared standard solution

The same CCV standard shall be used throughout the analysis runs for a Sample Delivery Group (SDG) of samples received.

9.5.2 Each CCV analyzed shall reflect the conditions of analysis of all associated analytical samples (the preceding 10 analytical samples or the preceding analytical samples up to the previous CCV). The duration of analysis, rinses, and other related operations that may affect the CCV measured result may not be applied to the CCV to a greater extent than the extent applied to the associated analytical samples. For instance, the difference in time between a CCV analysis and the blank immediately following it, as well as the difference in time between the CCV and the analytical sample immediately preceding it, may not exceed the lowest difference in time between any two consecutive analytical samples associated with the CCV.

9.5.3 Information regarding the CCV shall be reported on Form IIA-IN.

9.6 Initial and Continuing Calibration Blank (ICB/CCB)

A calibration blank shall be analyzed at the wavelength used for analysis immediately after every ICV and CCV, at a frequency of 10% or every 2 hours during the run, whichever is more frequent. The blank shall be analyzed at the beginning of the run and after the last analytical sample.

NOTE: A CCB shall be analyzed immediately after the last CCV, and the last CCV shall be analyzed immediately after the last analytical sample of the run. The results for the calibration blanks shall be reported on Form III-IN.

10.0 PROCEDURE

10.1 Sample Preparation

10.1.1 If insufficient sample amount (less than 90%, of the required amount) is received to perform the analyses, the Contractor shall contact Sample Management Office (SMO) to inform them of the problem. SMO will contact the Region for instructions. The Region will either require that no sample analyses be performed or will require that a reduced volume be used for the sample analysis. No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the Sample Delivery Group (SDG) Narrative.

10.1.2 If multi-phase samples (e.g., two-phase liquid sample, oily sludge/sandy soil sample) are received by the Contractor, the Contractor shall contact SMO to apprize them of the type of sample received. SMO will contact the Region. If all phases of the sample are amenable to analysis, the Region may require the Contractor to do any of the following:

- Mix the sample and analyze an aliquot from the homogenized sample.
- Separate the phases of the sample, and analyze one or more of the phases separately. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.1 If all of the phases are not amenable to analysis (i.e., outside scope), the Region may require the Contractor to do any of the following:

- Separate the phases and analyze the phase(s) that is (are) amenable to analysis. SMO will provide EPA sample numbers for the additional phases, if required.
- Do not analyze the sample.

10.1.2.2 No other changes in the analyses will be permitted. The Contractor shall document the Region's decision in the SDG Narrative.

10.1.3 Soil samples are not dried prior to analysis. A separate percent solids determination must be made in accordance with the procedure in Exhibit D - Introduction to Analytical Methods, Section 1.6.

10.1.4 Before preparation is initiated for an aqueous sample, the Contractor shall test for the presence of sulfides and oxidizing agents (e.g., residual chlorine). The test for sulfides shall be performed by placing a drop of the sample on a strip of lead acetate paper (which has been pre-moistened with pH 4 acetate buffer solution). If the test strip turns black, the Contractor shall treat the total volume of sample with powdered cadmium carbonate or lead carbonate. Yellow cadmium sulfide precipitates when the sample contains sulfide. This operation shall be repeated until a drop of the treated sample solution does not darken the lead acetate test paper. The solution shall be filtered through a dry filter paper into a dry beaker, and the volume of sample to be used for analysis shall be measured from the filtrate. It is recommended that the Contractor avoid a large excess of cadmium carbonate and a long contact time in order to minimize a loss by complexation or occlusion of cyanide on the

precipitated material. The test for oxidizing agents shall be performed by placing a drop of the sample on a strip of potassium iodide - starch test paper (KI - starch paper). If the test strip turns blue, the Contractor shall contact SMO for further instructions from the Region before proceeding with sample preparation and analysis. The Contractor shall document the presence of sulfides or oxidizing agents in the SDG Narrative.

10.2 Water and Soil Preparation of Standards and Samples

10.2.1 Standards Preparation

10.2.1.1 It is not imperative that all standards be distilled in the same manner as the samples. At least one standard (mid-range) must be distilled and compared to similar values on the curve to ensure that the distillation technique is reliable. The mid-range standard must be analyzed immediately after the first CCV/CCB. If the distilled standard does not agree within ±15% of the undistilled standards, the operator shall find and correct the cause of the apparent error before proceeding.

10.2.1.2 Standards for Manual Spectrophotometric Analysis of Water and Soil Samples

Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 250 milliliter (mL) volumetric flasks.

NOTE: The concentration of one of the calibration standards shall be at the Contract Required Quantitation Limit (CRQL).

To each standard, add 50 mL of 1.25N NaOH and dilute to 250 mL with reagent water. The same method for color development (i.e., pyridine-barbituric acid or pyridine-pyrazolone) must be used for both the samples and standards. Standards must bracket the concentration of the samples. If dilution is required, use the blank solution.

10.2.1.3 Standards for Semi-Automated Spectrophotometric Analysis of Water and Soil Samples

Calibration standards - Prepare a blank and at least three calibration standards over the range of the analysis by pipetting suitable volumes of standard solution into volumetric flasks. One calibration standard must be at the CRQL. Add NaOH to each standard to bring the concentration of NaOH to 10 grams per Liter (g/L). Store at 4°C (±2°C).

10.2.1.4 Standards for Midi Distillation Preparation and Semi-Automated Spectrophotometric Analysis of Water and Soil Samples

Prepare a minimum of three standards and a blank by pipetting suitable volumes of standard solution into 50 mL volumetric flasks. Dilute standards to 50 mL with 0.25N NaOH.

NOTE: One calibration standard must be at the CRQL.

10.2.2 Water Samples Preparation (Distillation)

10.2.2.1 Preparation Method/Code (DW1)

10.2.2.1.1 Place 500 mL of sample in the 1 liter boiling flask. Add 50 mL of NaOH solution (see Section 7.1.2.1) to the absorbing tube and dilute if necessary with reagent water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber and trap in the train.

10.2.2.1.2 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to re-adjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

10.2.2.1.3 Slowly add 25 mL concentrated sulfuric acid (H_2SO_4) (see Section 7.1.2.4) through the air inlet tube. Rinse the tube with reagent water and allow the airflow to mix the flask contents for three minutes. Pour 20 mL of magnesium chloride solution (see Section 7.1.2.6) into the air inlet and wash down with a stream of water.

10.2.2.1.4 Heat the solution to boiling, taking care to prevent the solution from backing up into and overflowing from the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

10.2.2.1.5 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with reagent water washings from the absorber tube.

NOTE: The distillation procedure results in a two-fold concentration of the sample.

10.2.3 Water Samples Preparation (Midi-Distillation)

10.2.3.1 Preparation Method/Code (DW2)

10.2.3.1.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 50 mL or less for aqueous samples.

10.2.3.1.2 Pipet 50 mL of sample, or an aliquot diluted to 50 mL, into the distillation flask along with 2 or 3 boiling chips.

10.2.3.1.3 Add 50 mL of 0.25N NaOH (see Section 7.1.3.1) to the gas absorbing impinger.

10.2.3.1.4 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N NaOH.

10.2.3.1.5 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of three bubbles per second from the impingers in each reaction vessel.

10.2.3.1.6 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (see Section 7.1.3.2) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.2.3.1.7 Add 2 mL of magnesium chloride solution (see Section 7.1.2.6) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.3.1.8 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.3.1.9 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.2.3.1.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section 8.3.

10.2.4 Soil Samples Preparation

10.2.4.1 Preparation Method/Code (DS1) (Distillation)

10.2.4.1.1 Accurately weigh a representative 1-5 gram (g) portion of wet sample and transfer it to a boiling flask. Add 500 mL of reagent water. Shake or stir the sample so that it is dispersed.

10.2.4.1.2 Add 50 mL of NaOH solution (see Section 7.1.2.1) to the absorbing tube and dilute if necessary with reagent water to obtain an adequate depth of liquid in the absorber. Connect the boiling flask, condenser, absorber, and trap in the train.

10.2.4.1.3 Start a slow stream of air entering the boiling flask by adjusting the vacuum source. Adjust the vacuum so that approximately one bubble of air per second enters the boiling flask through the air inlet tube.

NOTE: The bubble rate will not remain constant after the reagents have been added and while heat is being applied to the flask. It will be necessary to re-adjust the air rate occasionally to prevent the solution in the boiling flask from backing up into the air inlet tube.

10.2.4.1.4 Slowly add 25 mL of concentrated H_2SO_4 (see Section 7.1.2.4) through the air inlet tube. Rinse the tube with reagent water and allow the airflow to mix the flask contents for 3 minutes. Pour 20 mL of magnesium chloride solution (see Section 7.1.2.6) into the air inlet and wash down with a stream of water.

10.2.4.1.5 Heat the solution to boiling, taking care to prevent the solution from backing up and overflowing into the air inlet tube. Reflux for one hour. Turn off heat and continue the airflow for at least 15 minutes. After cooling the boiling flask, disconnect absorber and close off the vacuum source.

10.2.4.1.6 Drain the solution from the absorber into a 250 mL volumetric flask and bring up to volume with reagent water washings from the absorber tube.

10.2.4.2 Preparation Method/Code (DS2) (Midi-Distillation)

10.2.4.2.1 The procedure described here utilizes a midi distillation apparatus and requires a sample aliquot of 1 gram for solid materials.

10.2.4.2.2 Weigh 1.0 g of sample (to the nearest 0.01 g) into the distillation flask and dilute to 50 mL with reagent water. Add 2 or 3 boiling chips.

10.2.4.2.3 Add 50 mL of 0.25N NaOH (see Section 7.1.3.1) to the gas absorbing impinger.

10.2.4.2.4 Connect the boiling flask, condenser, and absorber in the train. The excess cyanide trap contains 0.5N NaOH.

10.2.4.2.5 Turn on the vacuum and adjust the gang (Whitney) valves to give a flow of three bubbles per second from the impingers in each reaction vessel.

10.2.4.2.6 After five minutes of vacuum flow, inject 5 mL of 50% (v/v) H_2SO_4 (see Section 7.1.3.2) through the top air inlet tube of the distillation head into the reaction vessel. Allow to mix for 5 minutes.

NOTE: The acid volume must be sufficient to bring the sample/solution pH to below 2.0.

10.2.4.2.7 Add 2 mL of magnesium chloride solution (see Section 7.1.2.6) through the top air inlet tube of the distillation head into the reaction flask. Excessive foaming from samples containing surfactants may be quelled by the addition of either another 2 mL of magnesium chloride solution or a few drops of a commercially available anti-foam agent. The Contractor shall document the addition of magnesium chloride solution or anti-foam agent in the SDG Narrative.

10.2.4.2.8 Turn on the heating block and set for 123-125°C. Heat the solution to boiling, taking care to prevent solution backup by periodic adjustment of the vacuum flow.

10.2.4.2.9 After one and a half hours of refluxing, turn off the heat and continue the vacuum for an additional 15 minutes. The flasks should be cool at this time.

10.2.4.2.10 After cooling, close off the vacuum at the gang valve and remove the absorber. Seal the receiving solutions and store them at 4°C until analyzed. The solutions must be analyzed for cyanide within the 12 day holding time specified in Section 8.3.

10.2.5 Non-Distilled Analyses

10.2.5.1 Preparation Method/Code (NP1)

10.2.5.1.1 This code shall be used to report samples that are not distilled prior to analysis.

10.2.5.1.2 This Preparation Method/Code shall also be used to report the non-distilled Method Detection Limit (MDL). The concentration of this MDL shall be used to determine the appropriate concentration qualifier for the results of instrument QC analyses [except the distilled Initial Calibration Verification (ICV)].

10.3 Sample Analysis

10.3.1 Manual Spectrophotometric Determination

10.3.1.1 Allow all standards and samples to come to ambient room temperature prior to analysis. Withdraw 50 mL or less of the solution from the flask and transfer to a 100 mL volumetric flask. If less than 50 mL is taken, dilute to 50 mL with 0.25N sodium hydroxide solution (see Section 7.1.3.1). Add 1.0 mL of acetate buffer (see Section 7.1.4.1) and mix. The dilution factor must be reported on Form XIII-IN.

10.3.1.2 Add 2 mL of chloramine-T (see Section 7.1.4.2) and mix. After 1 to 2 minutes, add 5 mL of pyridine-barbituric acid solution (see Section 7.1.4.3.1) and mix. Dilute to mark with reagent water and mix again. Allow 8 minutes for color development then read absorbance between 570 and 580 nanometers (nm) in a 1 centimeter (cm) cell within 15 minutes.

10.3.2 Semi-Automated Spectrophotometric Determination of Distillates

10.3.2.1 Set up the manifold. Pump the reagents through the system until a steady baseline is obtained.

10.3.2.2 Place calibration standards, blanks, and control standards in the sampler tray, followed by distilled samples, distilled duplicates, distilled standards, distilled spikes, and distilled blanks. Allow all standards and samples to come to ambient room temperature prior to analysis.

10.3.2.3 When a steady reagent baseline is obtained and before starting the sampler, adjust the baseline using the appropriate knob on the colorimeter. Aspirate a calibration standard and adjust the colorimeter until the desired signal is obtained. Establish the baseline and proceed to analyze calibration standards, blanks, control standards, distilled samples, and distilled Quality Control (QC) samples.

11.0 DATA ANALYSIS AND CALCULATIONS

11.1 Water/Aqueous Sample Calculation

11.1.1 For semi-automated colorimetric determination (Non-Midi-Distillation), measure the instrument response of the calibration standards and calculate a linear regression equation. Apply the equation to the samples and Quality Control (QC) samples to determine the cyanide concentration in the distillates. To determine the concentration of cyanide in the original sample, MULTIPLY THE RESULTS BY ONE-HALF (since the original volume was 500 milliliter (mL) and the distillate volume was 250 mL). Also correct for, and report on Form XIII-IN, any dilutions which were made before or after distillation.

11.1.2 For manual colorimetric determination, calculate the cyanide, in micrograms per Liter (µg/L), in the original sample as follows:

EQ. 1 Aqueous Sample Concentration (Manual)

$$\text{CN Concentration (µg/L)} = \frac{A \times 1000\ \text{mL/L}}{B} \times \frac{50\ \text{mL}}{C}$$

WHERE,

A	=	µg CN read from standard curve (per 250 mL)
B	=	mL of original sample for distillation (see Section 10.2.2.1.1)
C	=	mL taken for colorimetric analysis (see Section 10.3.1.1)
50 mL	=	volume of original sample aliquot (see Section 10.3.1.1)
1000 mL/L	=	conversion mL to L

The minimum value that can be substituted for A is the Method Detection Limit (MDL) value adjusted for volume.

11.2 Soil Sample Calculation

11.2.1 A separate determination of percent solids must be performed (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.2.2 The concentration of cyanide in the sample is determined as follows:

11.2.2.1 Manual Spectrophotometric

EQ. 2 Soil Sample Concentration (Manual)

$$\text{CN Concentration (mg/kg)} = \frac{A \times \frac{50\ \text{mL}}{B}}{C \times \frac{\%\ \text{solids}}{100}}$$

WHERE,

A	=	µg CN read from standard curve (per 250 mL).
B	=	mL of distillate taken for colorimetric determination (see Section 10.3.1.1).
C	=	wet weight of original sample in g (see Section 10.2.4.1.1).
50 mL	=	standard volume taken for colorimetric determination (see Section 10.3.1.1)
% solids	=	percent solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.2.2.2 Semi-Automated Spectrophotometric for Non-Midi-Distillates

If the semi-automated method is used, measure the peak heights of the calibration standards (visually or using a data system) and calculate a linear regression equation. Apply the equation to the samples and QC audits to determine the cyanide concentration in the distillates.

EQ. 3 Soil Sample Concentration (Semi-automated)

$$\text{CN Concentration (mg/kg)} = \frac{A \times .25}{C \times \frac{\% \text{ solids}}{100}}$$

WHERE,

A	=	µg/L determined from standard curve.
C	=	wet weight of original sample in g (see Section 10.2.4.1.1).
.25	=	conversion factor for distillate final volume (see Section 10.2.4.1.6).
% solids	=	percent solids (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

The minimum value that can be substituted for A is the MDL value.

11.3 Calculations for Midi Distillation of Waters and Soils

11.3.1 Calculations for Semi-automated Colorimetric Determination

11.3.1.1 Prepare a standard curve by plotting absorbance (peak heights, determined visually or using a data system) of standards (y) versus cyanide concentration values (total µg CN/L) (x). Perform a linear regression analysis.

11.3.1.2 Multiply all distilled values by the standardization value to correct for the stock cyanide solution not being exactly 1000 milligrams per Liter (mg/L) (see Section 7.2.2.2.1).

11.3.1.3 Using the regression analysis equation, calculate sample receiving solution concentrations from the calibration curve.

11.3.1.4 Calculate the cyanide of aqueous samples in µg/L of original sample, as follows:

EQ. 4 Aqueous Sample Concentration (Midi)

$$\text{CN Concentration (µg/L)} = \frac{A \times D \times F}{B}$$

WHERE,

A = µg/L CN of sample from regression analysis

B = volume of original sample for distillation (0.050 L) (see Section 10.2.3.1.2)

D = any dilution factor necessary to bracket sample value within standard values

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is the MDL value.

11.3.1.5 Calculate the cyanide of solid samples in mg/kg of original sample, as follows:

11.3.1.5.1 A separate determination of percent solids must be performed (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

11.3.1.5.2 The concentration of cyanide in the sample is determined as follows:

EQ. 5 Soil Sample Concentration (Midi)

$$\text{CN Concentration (mg/kg)} = \frac{A \times D \times F}{B \times E}$$

WHERE,

A = µg/L CN of sample from regression analysis curve

B = wet weight of original sample (see Section 10.2.4.2.2)

D = any dilution factor necessary to bracket sample value within standard values

E = % solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6)

F = sample receiving solution volume (0.050 L)

The minimum value that can be substituted for A is the MDL value.

11.4 Adjusted Method Detection Limit (MDL)/Adjusted Contract Required Quantitation Limit (CRQL) Calculation

To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for the manual colorimetric method, multiply the MDL (µg/L) or CRQL (µg/L) by

0.25 and substitute the result for the "A" term in Equation 1. To calculate the adjusted aqueous MDL or adjusted aqueous CRQL for all other methods, follow the instructions in Section 11.1.1 or substitute the MDL (µg/L) or CRQL (µg/L) for the "A" term in Equation 4, as appropriate.

The adjusted soil MDL or adjusted soil CRQL for all methods shall be calculated as follows:

EQ. 6 Adjusted Soil MDL/Adjusted Soil CRQL Concentration

$$\text{Adjusted Concentration (mg/kg)} = C \times \frac{W_M}{W_R} \times \frac{1}{S}$$

WHERE,

C	=	MDL or CRQL concentration (mg/kg)
W_M	=	minimum method required wet sample weight (g)
W_R	=	reported wet sample weight (g)
S	=	% Solids/100 (see Exhibit D - Introduction to Analytical Methods, Section 1.6).

For the midi-distillation, multiply the adjusted concentration value (mg/kg) obtained in Equation 6 by any applicable dilution factor.

12.0 QUALITY CONTROL (QC)

12.1 Initial Calibration Verification (ICV)

The ICV standard shall be prepared in the same matrix as the calibration standards and in accordance with the instructions provided by the supplier. The ICV standard shall be distilled. If measurements exceed the control limits of 85% (low) and 115% (high), the analysis shall be terminated, the problem corrected, the instrument recalibrated, and the calibration reverified. Information regarding the ICV shall be reported on Form IIA-IN.

12.2 Continuing Calibration Verification (CCV)

The CCV standard shall be prepared by the analyst at a concentration equivalent to the mid-point of the calibration curve. If the deviation of the CCV is greater than the control limits of 85% (low) and 115% (high), the analysis shall be stopped, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical samples analyzed since the last compliant calibration verification shall be performed. Information regarding the CCV shall be reported on Form IIA-IN.

12.3 Contract Required Quantitation Limit (CRQL) Check Standard (CRI)

12.3.1 To verify linearity near the CRQL, a standard at the CRQL (CRI) shall be prepared, in the same matrix as the calibration standards, and analyzed at the beginning and at the end of each sample analysis run, immediately following the ICV/ICB. In addition, the Contractor shall analyze the CRI at a frequency of not less than once per 20 analytical samples[1] per analysis run. The CRI analysis shall be run immediately followed by the CCV and Continuing Calibration Blank (CCB) analyses. The CRI shall be prepared by spiking an aliquot of reagent water with cyanide to yield a concentration in the final solution equal to the CRQL.

12.3.2 CRI and percent recovery results shall be reported on Form IIB-IN. If the percent recovery falls outside the control limits of 70-130%, the CRI shall be re-analyzed immediately. If the result of the re-analysis falls within the control limits, no further corrective action is required. If the result of the re-analysis does not fall within the control limits, the analysis shall be terminated, the problem corrected, the instrument recalibrated, the CRI analyzed, and the samples associated with the CRI re-analyzed.

12.4 Blank Analyses

There are two different types of blanks required by this method. The calibration blank is used in establishing the analytical curve while the preparation blank is used to monitor for possible contamination.

12.4.1 Initial and Continuing Calibration Blank (ICB/CCB)

The ICB and CCB are prepared with reagents and reagent water. If the absolute value of the calibration blank (ICB/CCB) result exceeds the CRQL (see Exhibit C), the analysis shall be terminated, the problem corrected, the instrument recalibrated, the calibration verified, and re-analysis of the preceding 10 analytical samples or all analytical

[1]As defined in Exhibit G, CRI is an analytical sample.

samples analyzed since the last compliant calibration blank shall be performed.

12.4.2 Preparation Blank (PB)

12.4.2.1 The PB shall contain all the reagents and in the same volumes as used in processing the samples. The PB shall be carried through the complete procedure and contain the same concentration in the final solution as the sample solution used for analysis.

12.4.2.2 At least one PB, consisting of reagent water processed through each sample preparation and analysis procedure (see Section 10), shall be prepared and analyzed with every Sample Delivery Group (SDG), or with each batch[2] of samples distilled, whichever is more frequent.

12.4.2.3 The first batch of samples in an SDG is to be assigned to Preparation Blank one, the second batch of samples to Preparation Blank two, etc. (see Form III-IN). Each Sample Data Package shall contain the results of all the PB analyses associated with the samples in that SDG.

12.4.2.4 The PB is to be reported for each SDG and used in all analyses to ascertain whether sample concentrations reflect contamination in the following manner:

12.4.2.4.1 If the absolute value of the concentration of the blank is less than or equal to the CRQL (see Exhibit C), no further action is required.

12.4.2.4.2 If the analyte concentration in the blank is above the CRQL, the lowest concentration of the analyte in the associated samples shall be greater than or equal to 10 times the blank concentration. Otherwise, all samples associated with the blank, with the analyte concentration less than 10 times the blank concentration and above the CRQL, shall be redistilled and re-analyzed with appropriate new QC. The only exception to this shall be an identified field blank. The sample concentration is not to be corrected for the blank value.

12.4.2.4.3 If the concentration of the blank is below the negative CRQL, then all samples associated with the blank and reported below 10 times CRQL shall be reprepared and re-analyzed with appropriate new QC.

The values for the preparation blank shall be reported on Form III-IN.

12.5 Spike Sample Analysis

12.5.1 The spike sample analysis is designed to provide information about the effect of the sample matrix on the distillation and/or measurement methodology. The spike is added prior to any distillation steps. At least one spike sample analysis (matrix spike) shall be performed on each group of samples of a similar

[2]A group of samples prepared at the same time.

matrix type (i.e., water, soil) or for each SDG.[3] The sample and its associated spike sample shall initially be run at the same dilution.

12.5.2 If the spike analysis is performed on the same sample that is chosen for the duplicate sample analysis, spike calculations shall be performed using the results of the sample designated as the "original sample" (see Section 12.6). The average of the duplicate results cannot be used for the purpose of determining percent recovery. Samples identified as field blanks and Performance Evaluation (PE) samples shall not be used for spiked sample analysis. USEPA may require that a specific sample be used for the spike sample analysis.

12.5.3 The analyte spiking solution shall be added to yield a final concentration of 100 µg/L in the final sample solution prepared for analysis (i.e., post-distillation). The final volume of the sample after distillation shall be the basis for the amount of cyanide to be added as the spike. For instance, the full volume distillation procedure will require addition of 25 µg cyanide to the sample prior to distillation [based on the final distillate volume of 250 milliliter (mL)] to meet the specified spiking level; and the midi distillation procedure requires the addition of 5 µg of cyanide to the sample prior to distillation (based on the final distillate volume of 50 mL).

12.5.3.1 For soil samples, the final sample solution prepared for analysis (i.e., the distillate) shall contain cyanide spiked at a concentration of 100 µg/L regardless of the distillation procedure employed, or the amount of sample used for distillation. The final sample volume after distillation shall be used as the basis for the amount of cyanide to add as the spike. The units for reporting soil sample cyanide results shall be mg/kg. To convert from µg/L to mg/kg, the equation below shall be used:

EQ. 7 Conversion to mg/kg

$$\text{mg/kg} = \text{µg/L} \times \frac{\text{final distillate volume (L)}}{\text{sample weight (g)}}$$

12.5.4 If the spike recovery is not at or within the limits of 75-125%, the data of all samples received and associated with that spike sample and determined by the same analytical method shall be flagged with the letter "N" on Forms IA-IN and VA-IN. An exception to this rule is granted when the sample concentration exceeds the spike added concentration by a factor of four or more. In such an event, the data shall be reported unflagged even if the percent recovery does not meet the 75-125% recovery criteria.

12.5.5 When the matrix spike recovery falls outside the control limits and the sample result does not exceed 4 times the spike added, a post-distillation spike shall be performed. Note that if a post-distillation spike analysis is required, the same USEPA sample that was used for the matrix spike analysis shall be used for the post digestion spike analysis. Spike the unspiked aliquot of the sample at 2 times the indigenous level or 2 times CRQL, whichever is greater. Results of the post-distillation spike shall be reported on Form VB-IN.

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[3]USEPA may require additional spike sample analyses, upon USEPA Regional CLP Project Officer (CLP PO) request.

12.5.6 In the instance where there is more than one spike sample per matrix, per method, per SDG, if one spike sample recovery is not within contract criteria, flag all the samples of the same matrix and method in the SDG. Individual component percent recoveries are calculated as follows:

EQ. 8 Spike Percent Recovery

$$\% \text{ Recovery} = \frac{SSR - SR}{SA} \times 100$$

WHERE,

SSR = Spiked Sample Result

SR = Sample Result

SA = Spike Added

12.5.7 When the sample concentration is less than the Method Detection Limit (MDL), use SR = 0 only for purposes of calculating percent recovery. The Spike Sample Results (SSRs), Sample Results (SRs), Spike Added (SA), and percent recovery (positive or negative) shall be reported on Form VA-IN.

12.5.8 The units used for reporting spike sample results will be identical to those used for reporting sample results on Form IA-IN.

12.6 Duplicate Sample Analysis

12.6.1 One duplicate sample shall be analyzed from each group of samples of a similar matrix type (i.e., water, soil) or for each SDG.[4] Duplicates cannot be averaged for reporting on Form IA-IN. The sample and its associated duplicate sample shall initially be run at the same dilution.

12.6.2 Duplicate sample analyses are required for percent solids. Samples identified as field blanks and PE samples shall not be used for duplicate sample analysis. USEPA may require that a specific sample be used for duplicate sample analysis. The Relative Percent Difference (RPD) is calculated as follows:

EQ. 9 Duplicate Sample Relative Percent Difference

$$RPD = \frac{|S - D|}{(S+D)/2} \times 100$$

WHERE,

RPD = Relative Percent Difference

S = Sample Result (original)

D = Duplicate Result

12.6.3 The results of the duplicate sample analyses shall be reported on Form VI-IN. A control limit of 20% for RPD shall be used for

[4]USEPA may require additional duplicate sample analyses, upon USEPA Regional CLP PO request.

original and duplicate sample values greater than or equal to five times the CRQL (see Exhibit C). A control limit of the CRQL value shall be entered in the "Control Limit" column on Form VI-IN if either the sample or duplicate value is less than five times the CRQL. If the sample and duplicate values are greater than or equal to five times the CRQL, or if the sample and duplicate values are less than the CRQL, the "Control Limit" field is left empty.

12.6.4 If one result is above five times the CRQL level and the other is below, use the CRQL criteria to determine if the duplicate analysis is in control. If both sample and duplicate values are less than the MDL, the RPD is not calculated on Form VI-IN. For solid sample or solid duplicate results less than five times the CRQL, enter the value of the CRQL, corrected for sample weight and percent solids, (i.e., original, not duplicate sample weight and percent solids), in the "Control Limit" column. If the duplicate sample results are outside the control limits, flag all the data for samples received and associated with that duplicate sample with an "*" on Forms IA-IN and VI-IN. In the instance where there is more than one duplicate sample per SDG, if one duplicate result is not within contract criteria, flag all samples of the same matrix and method in the SDG. The percent difference data will be used by USEPA to evaluate the long-term precision of the method. Specific control limits for each element will be added to Form VI-IN at a later date based on the precision results.

12.7 Laboratory Control Sample (LCS) Analysis

12.7.1 A solid LCS (LCSS) shall be analyzed using the same sample preparations, analytical methods, and Quality Assurance (QA)/QC procedures employed for the EPA samples received. For cyanide, a distilled ICV shall be used as the aqueous LCS (LCSW).

12.7.2 The USEPA provided LCSS shall be prepared and analyzed using each of the procedures applied to the solid samples received (exception: percent solids determination not required). If the USEPA LCSS is unavailable, other USEPA QC Check samples or other certified materials may be used. In such a case, the control limits for LCSS must be documented and provided. One LCSS shall be prepared and analyzed for every group of solid samples in a SDG, or for each batch of samples distilled, whichever is more frequent.

12.7.3 All LCSS and percent recovery results will be reported on Form VII-IN. If the results for the LCSS fall outside the control limits established by USEPA, the analyses shall be terminated, the problem corrected, and the samples associated with that LCSS reprepared and re-analyzed with appropriate new QC.

12.8 Method Detection Limit (MDL) Determination

12.8.1 Before any field samples are analyzed under this contract, the MDLs shall be determined for non-distilled analyses (Preparation Method/Code "NP1") and for each distillation procedure and instrument used, prior to the start of the contract analyses, and annually thereafter, and shall meet the levels specified in Exhibit C.

An MDL study shall be performed after major instrument maintenance, or changes in instrumentation or instrumental conditions to verify the current sensitivity of the analysis.

12.8.2 To determine the MDLs, the Contractor shall run MDL studies following the procedures given in 40 CFR, Part 136. The Contractor shall

prepare the MDL samples by each distillation procedure used and shall analyze these samples on each instrument used. The Contractor shall also analyze the non-distilled MDL samples on each instrument used.

12.8.3 The determined concentration of the MDL shall be less than half the concentration of the CRQL listed in Exhibit C.

12.8.4 The non-distilled MDL (Preparation Method/Code "NP1") shall be used to determine the appropriate concentration qualifier for the results of instrument QC analyses (except the distilled ICV).

12.8.5 The results of the MDL determination study shall be forwarded to the USEPA Regional CLP PO, Sample Management Office (SMO), and Quality Assurance Technical Support (QATS).

12.8.6 The MDL results shall be reported on Form IX-IN.

12.9 Example Analytical Sequence for Cyanide

S0
S10.0
S50.0
S100.0
S200.0
S400.0
ICV (distilled)
ICB
CRI
CCV
CCB
MIDRANGE
9 samples
CCV
CCB
9 samples
CRI
CCV
CCB
10 samples, etc.

13.0 METHOD PERFORMANCE

Not applicable.

14.0 POLLUTION PREVENTION

See Section 1.15 in Exhibit D - Introduction to Analytical Methods.

15.0 WASTE MANAGEMENT

See Section 1.16 in Exhibit D - Introduction to Analytical Methods.

16.0 REFERENCES

16.1 US Environmental Protection Agency. Methods for Chemical Analysis of Water and Wastes. Method 335.2. 1980.

16.2 American Water Works Association/American Public Health Association/Water Environment Federation. Standard Methods for the Examination of Water and Wastewater. Method 4500. 18th Edition.

16.3 US Government Printing Office. 40 Code of Federal Regulations, Part 136, Section 1, Appendix B.

17.0 TABLES/DIAGRAMS/FLOWCHARTS

Not applicable.